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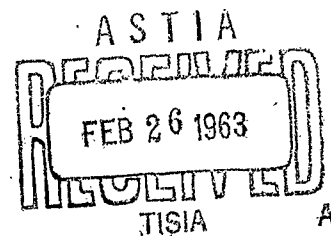
APPLICATIONS OF LOCALIZED PERTURBATION TECHNIQUE

by

M. Asgar Ali and Richard F. Wood

Quantum Chemistry Group
For Research in Atomic, Molecular and Solid-State Theory
Uppsala University, Uppsala, Sweden

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ABSTRACT

Applications have been made of the localized perturbation technique for conjugated systems within the framework of Hückel theory by using the inverse of cyclic matrices in closed analytical form in terms of Chebyshev polynomials by the method of Löwdin, Pauncz and de Heer. It is shown that by this approach, one can get the exact energy levels and eigenfunctions of perturbed conjugated systems by a simple non-iterative method for simple perturbations and by a second order iteration process for complicated perturbations which reduces the numerical "size" of the problem considerably. Possible applications of this technique in other related fields are discussed.

INTRODUCTION

In this technical note, we shall apply some of the methods developed by Löwdin ¹⁾ in sections VI and VII of the "Studies in Perturbation Theory" in an investigation of some properties of perturbed simple conjugated systems. These applications will illustrate the power and elegance of this new approach. Most of the results contained herein are not entirely new but the methods used have been recently developed and show promise of being particularly powerful when applied to more complex systems than those described here. Thus the emphasis shall be more on the techniques than on the results.

1) P.O. Löwdin, Technical Notes Nos. 64 and 65 from the Uppsala Quantum Chemistry Group.

We shall be working within the framework of the simple Hückel approximation, inspite of the well-known limitations of the theory which results therefrom. The justification for this severe restriction lies in the usefulness of simple Hückel theory in correlating diverse properties of conjugated systems, e.g. Coulson ^{2a)}, especially in finding out the biochemical potentiality of complex molecules and as a starting point for more sophisticated theories of the electronic structure of these molecules.

2a) C.A. Coulson, Symposium on Molecular Physics, Nikko, Japan (1953).

It is of great interest in this connection to note that recently Löwdin ^{2b)} generalizing certain ideas of Brueckner has shown, from the view-point of perturbation theory, how it is possible to obtain from the eigenfunctions of a "model Hamiltonian" of the Hückel type the exact eigenfunctions of the system including all many-particle interactions exactly by means of the reaction operator. Hence, in principle, we can pass from the eigenfunctions of the Hückel Hamiltonian to the exact eigenfunctions of the system, at least formally. So a simple and direct way of obtaining the eigensolutions of the Hückel Hamiltonian for conjugated systems would be of considerable value.

2b) P.O. Löwdin, Technical Notes Nos. 47 and 48 from the Uppsala Quantum Chemistry Group (1960); J. Math. Phys. 3, ... (1962).

A straightforward solution of the eigenvector and eigenvalues of the Hückel Hamiltonian for complicated molecules could be rather time-consuming, if the calculation has to be repeated for a range of values of the basic parameters which enter into the theory. By a perturbation approach, we can use maximally the already known information of the basic skeleton reducing the numerical magnitude of the problem considerably and yet, using the method of Löwdin obtaining the exact solutions which correspond to the use of the whole perturbation series.

In section I, we give a brief review of some of the important theoretical work done on the theory of simple conjugated systems in the past. Particular attention is devoted to the role played by the Hückel theory in the development of the present day approach to the calculations on these systems. This discussion is necessarily limited, and it is meant only to set the stage for the latter sections. Although we point out some of the successes and failures of the simple Hückel approach, the discussion is definitely not a critique of the theory.

In section II, we explain the two methods to be used and derive the important equations which we shall need later in the succeeding sections.

In section III, we illustrate the utility of the first or non-iterative method of the preceding section by applying it in the calculations of the eigenfunctions and eigenvectors of some locally perturbed ring type conjugated systems.

In section IV, we continue with the applications and demonstrate the second or iterative method by using it in calculations on simple conjugated systems of both chain and ring type.

In section V, we conclude by giving a brief discussion of the two methods and some of their possible applications.

I. REVIEW OF WORK ON CONJUGATED SYSTEMS

In 1931, Hückel ³⁾ applied the molecular orbital theory developed by Lennard-Jones, Hund and Mulliken in an investigation of the π -electron system of the benzene molecule. Hückel's approach to the problem can be characterized by two basic properties, i.e. the well-known σ - π separation of the electrons and the two-parameter nature of the theory which derives from the use of the so-called "coulomb" and "resonance" integrals usually denoted by α and β respectively. Since Hückel's original work, a substantial body of literature has developed around the application of the theory to conjugated systems. Hückel's theory, especially in its semi-empirical form, has been an extraordinarily useful tool for the correlation of mainly ground-state properties of conjugated and aromatic hydrocarbon molecules. The theory has led to a fundamental understanding of such properties as resonance stability, bond lengths, charge densities, free valence and the reactivity of these molecules to electrophilic, nucleophilic and free radical reagents. It is still not clearly understood why the Hückel theory is so successful although Hall ^{4a)} has pointed out that it is most likely due to a remarkable correspondence to a more sophisticated approach rather than to the validity of the many assumptions inherent in the theory. Löwdin ^{2b)} has also pointed out that in the Hückel theory, the Hamiltonian operator is not actually specified and this remarkable success might mean that the two-parameter Hamiltonian matrix may correspond to the use of the exact effective Hamiltonian operator including all many-body interactions exactly. It is also of interest to mention that several authors ^{4b)} have pointed out that indices like Coulson charges and bond orders and polarizabilities which are used to characterize the properties are precisely those which would be the relevant indices for the molecule from a consideration of the one-particle density matrix of the molecule. So certain measure of the success of Hückel theory is due to the fact that we are dealing with

³⁾ E. Hückel, Z. Physik 70, 204 (1931).

^{4a)} G.G. Hall, Proc. Roy. Soc. (London) A213, 102, 113 (1952).

^{4b)} P.O. Löwdin, Proc. Int. Conf. Theor. Physics, Japan, Kyoto 1953, p. 599; Phys. Rev. 97, 1490 (1955); R. McWeeny, Proc. Roy. Soc. (London) A232, 114 (1955).

the right type of indices for these molecules. Pople's calculations ⁵⁾ on the ground state of aromatic hydrocarbons by SCF MO theory seems to justify this conclusion. Pople made a number of approximations which had the effect of making the SCF LCAO MO equations of Roothaan ⁶⁾ simpler and more amenable to solution. He also showed that these modified equations, when applied to alternant hydrocarbons, had the same form as the equations of Hückel theory plus some perturbation terms due to explicit inclusion of electron interaction and that the SCF charge distribution in the ground state of alternant hydrocarbons is as uniform as in Hückel theory.

The applicability of the Hückel method can be extended to hetero-systems ⁷⁾ like pyridine by introducing a "coulomb parameter" appropriate for the substituted atom and an "inductive parameter" which is meant to account for the change of electronegativity of the carbon atoms adjacent to heteroatoms. From detailed calculations on pyridine, Wheland and Pauling ⁸⁾ concluded that the value of the inductive parameter must be approximately one tenth of the coulomb parameter to explain the orientation in reactions of pyridine and in later works, this ratio or a value close to it has been used extensively. In recent years and in light of more refined calculations of an SCF type such as those reported by McWeeny and Peacock ⁹⁾ and by Brown and Heffernan ¹⁰⁾ considerable doubt has been cast on the validity of using the inductive parameter originally introduced by Wheland and Pauling.

Coulson and Rushbrooke ¹¹⁾ showed that the Hückel theory within its initial approximations is internally self-consistent when applied to alternant hydrocarbons. By self-consistent it is meant that the assumption that all of the diagonal elements of the Hamiltonian matrix are equal leads to the conclusion that in the ground state, the Coulson charges of the individual atoms are all equal and thus does not contradict the original assumption.

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- 5) J.A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
- 6) C.C.J. Roothaan, Revs. Modern Phys. 23, 69 (1951).
- 7) E. Hückel, Z. Physik 12, 310 (1931); 16, 628 (1932).
- 8) G.W. Wheland and L. Pauling, J. Am. Chem. Soc. 57, 2086 (1935).
- 9) R. McWeeny and T.E. Peacock, Proc. Phys. Soc. ALXX, 41 (1957).
- 10) R.D. Brown and M.L. Heffernan, Australian J. Chem. 10, 211 (1957).
- 11) C.A. Coulson and G.S. Rushbrooke, Proc. Cambridge Phil. Soc. 36, 193 (1910).

Coulson and Longuet-Higgins ^{12a)} in a series of papers generalized the ideas of Wheland and Pauling and developed a second order perturbation theory for conjugated systems. They derived some very basic theorems concerning the total charge orders and bond orders of the π -electron system and defined certain polarizability coefficients. These coefficients have proved extremely useful in understanding the chemical reactivity and the changes produced in the properties of a conjugated molecule on substitution of a carbon atom by a heteroatom. Longuet-Higgins ^{12b)} has applied these polarizability coefficients in an understanding of the basic properties of heteromolecules.

Löwdin ¹³⁾ has extended the theory and generalized the definition of charge orders and bond orders to account for the non-orthogonality of the basic atomic orbitals. He also emphasized the importance of the charge orders and bond orders of the individual molecular orbitals.

The choice of the value to assign for the coulomb parameter of the substituted atom has always been a problem. Wheland and Pauling based their choice on consideration of the electronegativity differences between the heteroatom and carbon atom and both the Pauling ¹⁴⁾ and Mulliken ¹⁵⁾ scales of electronegativity have been used. It is evident now that the value of the coulomb parameter which should be assigned depends on the physical quantity under consideration. Thus one value of the coulomb parameter will give good agreement with reactivity data whereas a rather different value is necessary if agreement with dipole moment data is sought. Illustrations of this fact are numerous in the literature but we might mention the calculations of Longuet-Higgins and Coulson ¹⁶⁾, Orgel et al ¹⁷⁾, Löwdin ¹⁸⁾,

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- 12a) C.A. Coulson and H.C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947); A192, 16 (1947); A193, 447, 456 (1948); A195, 188 (1948).
 - 12b) H.C. Longuet-Higgins, J. Chem. Phys. 18, 275 (1950).
 - 13) P.O. Löwdin, J. Chem. Phys. 21, 496 (1953).
 - 14) L. Pauling, J. Am. Chem. Soc. 54, 3570 (1932).
 - 15) R.S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573 (1935).
 - 16) H.C. Longuet-Higgins and C.A. Coulson, Trans. Faraday Soc. 43, 87 (1947).
 - 17) Orgel, Cottrell, Dick and Sutton, Trans. Faraday Soc. 47, 113 (1951).
 - 18) Reference 13.

Lofthus ¹⁹⁾ and Hamerka and Liquori ²⁰⁾. It is, however, desirable theoretically that with one particular value of the parameter we should be able to interpret the diverse properties of heteromolecules.

The most recent tendency has been to carry out some type of SCF CI calculations for the π -electrons with integral approximations of the type introduced by Pariser and Parr ²¹⁾ and then to choose the parameters in Hückel theory in such a way that the SCF results for the charge densities in the ground state are reproduced. The calculations reported in references 9 and 10 are of this type and Amos and Hall ²²⁾ have reported a similar type of calculation. The results have led to the conclusion that the value of the coulomb parameter for nitrogen, for example, in pyridine-like systems should be between 0.2 and 0.4 in order to reproduce the SCF results.

The simple Hückel theory, so useful for the correlation of ground state properties, cannot adequately describe excited states. Thus, it is not possible to explain the spectra of benzene, pyridine and the disubstituted benzene molecules on the basis of the naive idea of transitions between the filled and unfilled Hückel molecular orbitals. In order to obtain agreement with the experimental results on the spectra of these molecules, it is necessary to carry out rather elaborate calculations. Longuet-Higgins ²³⁾ has discussed the excited state calculations in a review article and here we shall mention only two of the problems.

Coulson ²⁴⁾ showed that the calculated electronic spectra of the polyacenes could be made more consistent with the calculated ground state properties if one took into account the overlap integral between neighbouring carbon atoms instead of neglecting it as Hückel originally did.

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- 19) A. Lofthus, *Molecular Physics* 1, 9 (1958).
20) H.F. Hamerka and A.M. Liquori, *Molecular Physics* 2, 367 (1959).
21) R. Pariser and R.G. Parr, *J. Chem. Phys.* 21, 466, 767 (1953).
22) A.T. Amos and G.G. Hall, *Molecular Physics* 4, 25 (1961).
23) H.C. Longuet-Higgins, *Advances in Chemical Physics* 1, 239 (1958).
24) C.A. Coulson, *Proc. Phys. Soc. (London)* A68, 81 (1955).

The inclusion of overlap had the effect of distributing the energy of the unoccupied molecular orbitals wider and compressing the occupied molecular orbitals in energy scale which leads to a slightly better understanding of the spectra of polyacenes, the spectra being interpreted to be due to one electron jumps from occupied Hückel molecular orbitals to unoccupied ones. A study of the problem of inclusion of overlap was made by Löwdin ^{25a)} and later by Chirgwin and Coulson ^{25b)}, and the former showed that overlap could be included by carrying out a symmetric orthogonalization of the basis functions which induces a linear transformation of the Hamiltonian matrix. He also pointed out that the off-diagonal elements of the transformed Hamiltonian matrix are invariant to shift of the origin of energy while those of the original overlap neglected Hamiltonian matrix are not, and therefore any parametrization of the Hamiltonian matrix must be on the transformed Hamiltonian matrix, rather than on the original Hamiltonian matrix, as is usually done. The case of heteroatoms has further been studied by Del Re ^{25c)}.

Although the inclusion of overlap can improve the excited singlet states, the problem of triplet states remains until one attempts to take account of electron repulsion in a satisfactory manner. Unless electron repulsion is included in the calculations, the effects of overlap cannot be definitely determined as Pople ²⁶⁾ has shown.

Goeppert-Mayer and Sklar ²⁷⁾, very early (1938), tried to calculate the spectra of benzene using a Hamiltonian which included repulsion between the π -electrons. Their calculations led them to conclude, correctly, that the excited singlet levels were separated from each other and from the triplet levels by the electron repulsion terms, but numerical errors and the necessity of approximating many center integrals prevented them from obtaining accurate quantitative results. Following Goeppert-Mayer and Sklar, many people have worked on the theoretical calculations of the

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- 25a) P.O. Löwdin, Arkiv Math., Fys., Astr. 35A, No. 9 (1947);
J. Chem. Phys. 18, 365 (1950); Adv. Phys. 5, 1 (1956).
 - 25b) B.H. Chirgwin and C.A. Coulson, Proc. Roy. Soc. (London) A201,
196 (1950).
 - 25c) G. Del Re, Technical Note No. 20 from Uppsala Quantum Chemistry
Group (1958). Published in Nuovo Cimento 17, 644 (1960).
 - 26) J.A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
 - 27) M. Goeppert-Mayer and A.L. Sklar, J. Chem. Phys. 6, 645 (1938).

spectra of conjugated molecules. It is not possible for us to give an account of the development here but some of the most important work is contained in papers by Roothaan and Parr ²⁸⁾, Nira ²⁹⁾, Parr et al ³⁰⁾, Dewar and Longuet-Higgins ³¹⁾ and Pariser ³²⁾. Most of this work has been concerned with the problem of taking into account electron repulsion (between the individual π -electrons and between the σ and π electrons) in a satisfactory way.

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- 28) C.C.J. Roothaan and R.G. Parr, J. Chem. Phys. 17, 1001 (1949).
 - 29) K. Nira, J. Chem. Phys. 20, 1498 (1952).
 - 30) R.G. Parr, D.P. Craig and I.G. Ross, J. Chem. Phys. 18, 1561 (1950).
 - 31) M.J.S. Dewar and H.C. Longuet-Higgins, Proc. Phys. Soc. (London) A67, 795 (1954).
 - 32) R. Pariser, J. Chem. Phys. 24, 250 (1956).
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We quote from the review article by Longuet-Higgins mentioned above:

"It may be said, therefore, that the electronic spectra of aromatic hydrocarbons are now well understood. The essential features of the present theory are

(1) that, if suitable molecular orbitals are adopted in the determinant representing the wave function of the ground state, then the excited states may be adequately represented in terms of singly excited configurations alone, provided that,

(2) if the molecular orbitals are not self-consistent, then singly excited configurations contribute to the ground state and the unexcited configuration contribute to the excited states and provided also that,

(3) atomic orbital overlap is neglected and the integrals determining the matrix elements of the Hamiltonian are evaluated semi-empirically rather than by nonempirical calculation."

We have not yet mentioned either the method of alternant molecular orbitals (AMO) suggested by Löwdin ³³⁾ or the method of split p-orbitals

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- 33) P.O. Löwdin, Nikko Symp. Mol. Phys. (Maruzen, Tokyo 1954) p. 13; Phys. Rev. 97, 1509 (1955).

(SPO) introduced by Dewar and Wulfman ^{34a)}. In the former method, which is applicable to systems with an alternant character, electrons with plus spin are assigned to orbitals which have large amplitude at every alternate atom and small amplitude at the remaining atoms while electrons with minus spin are assigned to orbitals whose amplitude changes alternately but reversed to the former ones. Thus an attempt is made to incorporate electron correlation directly in the wave function. The principal idea of the SPO method is quite similar in that electron correlation is accounted for by constraining the electrons of different spin to be in different parts of space, in this case, the two lobes of the p-type atomic orbitals. It may be remarked that the SPO method has been criticized severely by Griffiths ^{34b)}.

Itoh and Yoshizumi ³⁵⁾ have applied the AMO method in the calculation of the ground state energy of benzene and have found that they could account for 85 o/o of the correlation error as determined by the Parr, Craig and Ross ³⁰⁾ calculation which was based on very extensive configuration interaction. Recently, Pauncz, de Heer and Löwdin ³⁶⁾ derived a general energy expression for an arbitrary alternant system with closed shell structure and made a numerical analysis of cyclic systems consisting of $2n = 4v + 2$ electrons moving in the field of $2n$ C-H centers. They arrived at the result that the energy depression decreases only slowly with increasing n and hence the method should be useful for large systems. Thus, it appears that the AMO method may indeed be a very simple device for including electron correlation in a particular class of molecules. The SPO method has been applied to ethylene by Dewar and Hojvat ³⁷⁾ with excellent results and calculations are reported to be underway on the ground state of benzene. It will be interesting to compare the results of the AMO and the SPO calculation on this molecule.

34a) M. J. S. Dewar and C. E. Wulfman, J. Chem. Phys. 29, 158 (1958).

34b) J. S. Griffiths, J. Chem. Phys. 36, 1689 (1962).

35) T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan 10, 201 (1955).

36) R. Pauncz, J. de Heer and P. O. Löwdin, Technical Notes Nos. 55 and 56 from Uppsala Quantum Chemistry Group (1960); published in J. Chem. Phys. 36, 2247, 2257 (1962).

37) M. J. S. Dewar and N. L. Hojvat, J. Chem. Phys. 34, 1232 (1961).

Actually, it seems to be quite possible that the two methods can be and should be combined (CAMO SPO) for the following reason. The AMO method accounts for correlation in the direction around the ring whereas the SPO method accounts for the correlation in a direction perpendicular to the plane of the molecule. Thus the situation here is analogous to the radial and angular correlation in atoms. Both types of correlation should be included simultaneously in any calculation if one wishes to determine the importance of one type compared to the other. It would seem to the authors that the calculations on the benzene molecule with the AMO approach probably over-emphasize the around-the-ring correlation.

Both the AMO and the SPO methods can be considered as special cases of the general idea of different orbitals for different spins which has been discussed frequently in the literature ³⁸⁾.

38) P.O. Löwdin, Phys. Rev. 97, 1509 (1955); Adv. Phys. 5, 1 (1956).

We shall conclude this section by giving a summary of the physical properties of interest in conjugated systems and the success or lack of success which simple Hückel theory has had in dealing with them.

a) Bond lengths.

The bond length is correlated with the calculated total π -bond order, P_{rs} , which is defined by

$$P_{rs} = \sum_j n_j c_{rj} c_{sj} \quad (1)$$

Here j runs over the occupied molecular orbitals, n_j is the occupation number of the j -th orbital and the c 's are the coefficients of the orbitals in the basis set. If r and s are not neighbours the bond order is taken to be zero. The correlation is carried out by drawing a bond length vs bond order curve based on several experimentally known points for a particular type of bond. This curve is then used to predict the bond length in other molecules containing the same type of bond. The Hückel theory is really quite successful in predicting the bond lengths of conjugated and aromatic molecules to an accuracy of about 0.02 Å which is sufficient for most practical purposes besides being almost at the limit of the accuracy of two

dimensional X-ray analysis. Detailed calculations by Coulson et al ³⁹⁾

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- 39) C.A. Coulson, R. Daudel and J.M. Robertson, Proc. Roy. Soc. A207, 306 (1951).
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have shown that configuration interaction and other refinements do not greatly alter the relative value of bond orders. The bond order is not very sensitive to the form of the wave function and thus, inspite of its great value in other respects, cannot be used as a criterion for a satisfactory wave function.

b) Charge Densities.

The π -electron charge density on any atom in a conjugated molecule is correlated with the total charge order which is given by

$$q_r = \sum n_j c_{jr}^2 \quad (2)$$

where the symbols have the same meaning here as in equation (1). The charge orders and bond orders form the elements of the charge and bond order matrix which for these systems, is twice the first order density matrix ^{40,41)} defined by

$$P = (CC^+)_{\text{occupied}} \quad (3)$$

The charge orders calculated with Hückel theory are sufficiently accurate to enable the chemist to predict the most probable position at which a charge reagent will attack the molecule.

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- 40) P.O. Löwdin, Phys. Rev. 97, 1474 (1955).

- 41) R. McWeeny, Revs. Modern Phys. 32, 335 (1960).
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c) Electric dipole moment.

The π -charge distribution calculated by Hückel theory can yield a qualitative understanding of the values of dipole moments among a series of molecules. In order to obtain correlation with experimental data it is necessary to choose values for the parameters which differ considerably from those values which give the best results for other physical properties. One must be careful, when treating dipole moment data, to take account of the contributions from lone pair electrons and from the σ -framework. The fact that the dipole moment is quite sensitive to small changes in the wave function which leave the energy almost unaffected further complicates the problem.

d) Orbital energies and spectra.

The simple Hückel theory is incapable of giving even satisfactory qualitative agreement with the experimental data on the spectra of conjugated systems.

II. DERIVATION OF EQUATIONS

We consider a system whose Hamiltonian operator can be written as

$$H = H_0 + V \quad (4)$$

and whose exact eigenfunction Ψ can be expanded in terms of a set of basis functions $\{\Phi_k\}$. The basis set can be chosen as orthonormal i.e.

$$\langle \Phi_k | \Phi_l \rangle = \delta_{kl} \quad (5)$$

We can carry out the usual transformation of the original eigenvalue equation $H\Psi = E\Psi$ into the matrix equation

$$(H_0 + V)C = EC \quad (6)$$

in which

$$(H_0)_{kl} = \langle \Phi_k | H_0 | \Phi_l \rangle, \quad V_{kl} = \langle \Phi_k | V | \Phi_l \rangle \quad (7)$$

and C is the column matrix whose elements are the expansion coefficients of Ψ in the basis set $\{\Phi_k\}$. Equation (6) can be rewritten in the form

$$C = (E\mathbb{I} - H_0)^{-1} V C \quad (8)$$

Following Löwdin in reference 1, we define

$$G \equiv (E\mathbb{I} - H_0)^{-1} \quad (9)$$

so that

$$C = GVC \quad \text{and} \quad C_k = \sum_{\alpha, \beta} G_{k\alpha} V_{\alpha\beta} C_\beta \quad (10)$$

If G can be obtained in closed form and if V is a matrix with only a few nonvanishing elements, some rather simple expressions for E can be derived. As an example, we can consider the case when only one element is non-vanishing, say, $V_{11} \neq 0$.

Equation (10) then becomes

$$C_i = G_{ii} V_{ii} C_i \quad \text{or} \quad G_{ii} = V_{ii}^{-1} \quad \text{if } C_i \neq 0 \quad (11)$$

and

$$C_k = G_{ki} V_{ii} C_i \quad (12)$$

Equation (11) has been used by Koster and Slater ⁴²⁾ and by Lax ⁴³⁾. The

42) G.F. Koster and J.C. Slater, Phys. Rev. 95, 1167 (1954).

43) M. Lax, Phys. Rev. 94, 1391 (1954).

former authors evaluated the matrix G by means of the transformation of H_0 to diagonal form, whereas Löwdin has pointed out that there are many alternative ways for evaluating this inverse matrix and that actually in many problems, the matrix itself is not needed but only the vector solution of a linear equation system.

The systems which we shall consider here all have the characteristic property that within the framework of simple Hückel theory, the matrix H_0 is cyclic or can be chosen as cyclic with suitable choice of the perturbation matrix V . It is customary to use only the "tight-binding approximation" or "nearest neighbour interaction", which we shall also use. This cyclic nature of H_0 allows us to find G by using the powerful method developed by Löwdin, Pauncz and de Heer ⁴⁴⁾ in a closed analytic form in terms of Chebyshev polynomials ⁴⁵⁾.

44) P.O. Löwdin, R. Pauncz, and J. de Heer, J. Math. Phys. 1, 461 (1960): It is interesting to note that E. Bodewig has used a similar technique (Matrix Calculus by E. Bodewig, North Holland Publishing Co., Amsterdam). However, he does not mention the fact that the polynomials which he introduces are actually nothing but the Chebyshev polynomials.

45) See appendix for a summary of the properties of these polynomials and refer to the "Tables of Chebyshev polynomials" published by National Bureau of Standards in their applied Mathematics Series for a more detailed discussion.

We shall now give a brief description of this method. The physical model which we have in mind during the discussion is that of a number, n , of atoms placed equidistant from each other on the circumference of a circle. Interactions between nearest neighbours only are considered. We must distinguish two cases a) an even number of atoms $n = 2v$ and b) an odd number $n = 2v + 1$.

a) $\underline{n = 2v}$

In this case, we use the equation (equation 34 of reference 44)

$$[M_1 + aI]^{-1} = \frac{1}{F_v(a)} \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(a) M_k \quad (13)$$

The M_k 's, which are cyclic and symmetric will be called topological matrices after Ruedenberg⁴⁶⁾ who has discussed M_1 . The matrix elements of M_1 , which we shall relate to our problem below, are given by

$$[M_1]_{pq} = \begin{cases} 1 & \text{if } p \text{ and } q \text{ are neighbours} \\ 0 & \text{otherwise} \end{cases} \quad (14)$$

It is somewhat easier to manipulate the M_k 's if these are expressed in terms of another type of elementary matrix. We write

$$M_k = m_k + m_{-k} \quad (15)$$

where

$$m_{-k} = m_k^{-1} = \tilde{m}_k \quad (16)$$

\tilde{m}_k is the transpose of m_k .

46) K. Ruedenberg, J. Chem. Phys. 34, 1884 (1961).

The elements of the m matrices are given by

$$[m_k]_{pl} = \delta_{(p+k)', l} \text{ and } [\tilde{m}_k]_{pl} = \delta_{(l+k)', p} \quad (17)$$

The prime is to remind us of the cyclic nature of the problem and simply means that if $(p+k)$ is outside of the range $1 \leq (p+k) \leq n$ we add n if $(p+k) < 1$ and subtract n if $(p+k) > n$, e.g. if $n = 10$, $k = 2$ and $p = 9$ then $\delta_{(11)',1} = \delta_{1,1}$.

The $\mathcal{L}_v(a)$ are the Chebyshev polynomials of the first kind (see appendix) and $F_v(a)$ is defined by

$$F_v(a) = \mathcal{L}_{v+1}(a) - \mathcal{L}_{v-1}(a) \quad (18)$$

Also, $\epsilon_0 = \epsilon_v = \frac{1}{2}$ and all other $\epsilon_k = 1$.

b) $n = 2v + 1$ 47)

Here we use the equation (equation 43 of reference 44)

$$[M_1 + a\mathbb{1}]^{-1} = \frac{1}{G_v(a)} \sum_{k=0}^v (-1)^k \eta_k \bar{D}_{v-k}(a) M_k \quad (19)$$

47) We use the Chebyshev polynomials of the first kind in this formulation but it is often more convenient to use the polynomials of the second kind as we shall do in Section IV.

with

$$\bar{G}_v = F_{v+1} - F_v \quad \text{and} \quad \bar{D}_v = \mathcal{L}_{v+1} - \mathcal{L}_v \quad (20)$$

$\eta_0 = \frac{1}{2}$ and all other η_k (including η_v) are equal to 1.

According to the assumptions of simple Hückel theory, $(H_0)_{kk} = \alpha$, $(H_0)_{k,(k+1)'} = (H_0)_{(k+1)',k} = \beta$ and all other elements of H_0 are zero. α and β are parameters which are usually determined empirically. Using these quantities we can write

$$G \equiv (E\mathbb{1} - H_0)^{-1} = -\frac{1}{\beta} (M_1 + a\mathbb{1})^{-1} \quad (21)$$

where

$$\alpha = \frac{E - \alpha}{-\beta} \quad (22)$$

Equation (8) now becomes

$$C = -\frac{1}{\beta} (M_1 + \alpha I)^{-1} V C \quad (23)$$

This equation can be made much simpler if the energy is expressed in units of β . Then equation (23) becomes

$$C = - (M_1 + \alpha I)^{-1} V C \quad (23a)$$

Now from equation 13, we have

$$[GV]_{ij} = -\frac{1}{F_v(\alpha)} \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(\alpha) \sum_{\gamma=1}^n (M_k)_{i\gamma} (V)_{\gamma j} \quad (24)$$

This can be written in terms of the m_k matrices, so that

$$[GV]_{ij} = -\frac{1}{F_v(\alpha)} \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(\alpha) \sum_{\gamma=1}^n (m_k + \tilde{m}_k)_{i\gamma} (V)_{\gamma j} \quad (25)$$

Using the properties of the m_k matrices, this becomes

$$[GV]_{ij} = -\frac{1}{F_v(\alpha)} \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(\alpha) \left\{ \sum_{\gamma=1}^n (\delta_{(i+k)', \gamma} + \delta_{(\gamma+k)', i}) (V)_{\gamma j} \right\} \quad (26)$$

Equation (10) now becomes

$$C_i = -\frac{1}{F_v(\alpha)} \sum_j \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(\alpha) \sum_{\gamma=1}^n (\delta_{(i+k)', \gamma} + \delta_{(\gamma+k)', i}) (V)_{\gamma j} C_j \quad (27)$$

and finally

$$C_i = -\frac{1}{F_v(\alpha)} \sum_j \sum_{k=0}^v (-1)^k \epsilon_k \zeta_{v-k}(\alpha) \left[V_{(i+k)', j} + V_{(i-k)', j} \right] C_j \quad (28)$$

This is the general equation for the case $n = 2v$ which we shall use later.

The corresponding equation for the case $n = 2v + 1$ is

$$C_i = -\frac{1}{F_v(\alpha)} \sum_j \sum_{k=0}^v (-1)^k \eta_k \bar{D}_{v-k}(\alpha) \left[V_{(i+k)', j} + V_{(i-k)', j} \right] C_j \quad (29)$$

These last two expressions give rise in application to equation systems whose order depends upon the number of nonvanishing matrix elements in the perturbation matrix V . The equation system is easily solved for one and two non-vanishing elements and frequently the symmetry of the problem makes it possible to solve a set of equations of order three. More complicated perturbation matrices give rise to equation systems which are treated better by a second order iteration-variation procedure ⁴⁸⁾. We shall now give a brief description of this method.

48) P.O. Löwdin, Technical Note No. 11, Uppsala Quantum Chemistry Group (1958), and the reference to the previous literature given there.

Following Löwdin ^{1, 48)}, we start from equation 10 and rewrite it as

$$(1 - GV)C = 0 \quad (30)$$

We note that $(1 - GV)$ is non-hermitian. Since it is easier to apply partitioning techniques to a hermitian matrix, we multiply by V from the left and obtain

$$(V - VGV)C = 0 \quad \text{or} \quad NC = 0 \quad (31)$$

where $N \equiv V - VGV$ and $N = N^\dagger$ (32)

Next we partition the basis set $\{\Phi_k\}$ into two subsets $\underbrace{\Phi_1}_1$ $\underbrace{\Phi_2 \dots \Phi_n}_2$ and from equation (31) obtain the two equations

$$N_{11}c_1 + N_{12}c_2 = 0 \quad (33)$$

$$N_{21}c_1 + N_{22}c_2 = 0 \quad (34)$$

From these two equations we then obtain

$$(N_{11} - N_{12}N_{22}^{-1}N_{21})c_1 = 0 \quad (35)$$

If $c_1 \neq 0$

$$N_{11} - N_{12}N_{22}^{-1}N_{21} \equiv F(E) = 0 \quad (36)$$

This equation contains E implicitly and is best solved iteratively. The iteration procedure as shown by Löwdin in reference 48 corresponds to the application of the Newton-Raphson process to $F(E)$. Thus

$$E^* = E - \frac{F(E)}{F'(E)} \quad (37)$$

where the prime denotes differentiation with respect to E . Now

$$F'(E) = N'_{11} - N'_{16} N_{66}^{-1} N_{61} + N_{16} N_{66}^{-1} N'_{66} N_{66}^{-1} N_{61} - N_{16} N_{66}^{-1} N'_{61} \quad (38)$$

We can simplify this equation considerably by using equation (34) and its complex conjugate so that

$$F'(E) = N'_{11} + N'_{16} \frac{C_6}{c_1} + \frac{C_6^+}{c_1^*} N_{66} \frac{C_6}{c_1} + \frac{C_6^+ N_{61}}{c_1^*} \quad (39)$$

which can be written, very simply, as

$$F'(E) = \frac{C^+ N' C}{|c_1|^2} \quad (40)$$

Also

$$F(E) = N_{11} + N_{16} \frac{C_6}{c_1} = \frac{N_{11} c_1 + N_{16} C_6}{c_1} = \frac{[NC]_1}{c_1} \quad (41)$$

where the subscript means we take the first element of $[NC]$. Therefore, we have that

$$E^* = E - \frac{[NC]_1 |c_1|^2}{c_1 C^+ N' C} \quad (42)$$

Now from the definition of N and G we obtain

$$\begin{aligned} N' &= V(E\mathbb{1} - H)^{-1} \cdot \mathbb{1} \cdot (E\mathbb{1} - H)^{-1} V \\ &= V G G V = V G^2 V \end{aligned} \quad (43)$$

and therefore,

$$E^* = E - \frac{[V(\mathbb{1} - G V) C]_1 c_1^*}{C^+ V G^2 V C} \quad (44)$$

So the iteration procedure consists of choosing a trial value of E , say E_0 , (different from the eigenvalues of H_0) and solving the equation system (from equation 34)

$$C_b^{(1)} = -N_{bb}^{-1} N_{b1} c_1 \quad (45)$$

If we choose $c_1 = 1$, then

$$C_0 = \begin{pmatrix} 1 \\ C_b^{(1)} \end{pmatrix} \quad (46)$$

We get

$$E^* = E_0 - \frac{[V(1 - G_0 V)C_0]}{C_0^+ V G_0^2 V C_0} \quad (47)$$

where

$$G_0 = (E_0 I - H_0)^{-1} \quad (48)$$

We define $G_0 V C_0 \equiv d_0$ and notice that for the exact E , $G_0 V C_0 = C_0$. We can now unite the second order iteration formula as

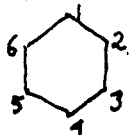
$$E^* = E_0 - \frac{[V(C_0 - d_0)]}{d_0^+ d_0} \quad (49)$$

In the perturbation of homocyclic conjugated systems to heterosystems, the perturbation usually involves only a few elements in the V matrix, so that the equation system to be solved will be of smaller order than that of the original problem. For example, for perturbations on three atoms, the equation system $NC = 0$ would give only three equations involving three coefficients only, and one of these coefficients can be determined from the normalization condition on C . This whole process is convenient if the matrix G can be found easily. Fortunately, all heterosystems both open chain and cyclic, can be achieved by suitable perturbations, diagonal or off-diagonal or both on a cyclic system. As we have seen above, the powerful method of Löwdin, Pauncz and de Heer is available for obtaining G for cyclic systems and it is this fact that leads to enormous simplification for the perturbation treatment.

III. PERTURBED RING SYSTEMS

In this section we shall treat various locally perturbed ring systems, particularly the mono-, di- and tri-substituted benzene ring by the first i.e. the non-iterative method outlined in the previous section. Here we shall consider only simple perturbations with two and three non-zero elements at most in the perturbation matrix. We shall neglect the non-diagonal inductive effects for the present but in a later section we shall show how they can be taken into account, approximately by first order perturbation theory within the framework of the non-iterative method. It is not our intention to relate our results to the physical properties of any real molecule; we wish only to illustrate the method and to set forth certain relationships and data which we believe may be useful in later studies. We shall treat the mono-substituted six membered ring rather thoroughly and only indicate how some of the results can be obtained for the more complicated perturbations and systems.

For reference purposes, we give first the Hückel theory result for benzene. There are two non-degenerate levels given by $\alpha + 2\beta$ and two doubly degenerate levels given by $\alpha + \beta$ where α and β are the coulomb and exchange parameters, respectively. The lowest three levels are doubly occupied and the other levels unoccupied in the ground state. The eigenvalues and eigenvectors are shown in Table I. The ϕ 's are the atomic orbitals and the numbering scheme is given by



It should be kept in mind that β is negative and therefore, $\alpha + 2\beta$ is the lowest level.

TABLE I. Eigenvalues and eigenvectors of benzene.

$T \equiv -1$.

Level	Energy	Eigenfunction	Symmetry
C	$\alpha + 2\beta$	$(6)^{-\frac{1}{2}} (1 \ 1 \ 1 \ 1 \ 1 \ 1)$	a_{2u}
B	$\alpha + \beta$	$(12)^{-\frac{1}{2}} (2 \ 1 \ \bar{1} \ 2 \ \bar{1} \ \bar{1})$	e_{1g}
A	$\alpha + \beta$	$(4)^{-\frac{1}{2}} (0 \ 1 \ 1 \ 0 \ \bar{1} \ \bar{1})$	e_{1g}
A'	$\alpha - \beta$	$(12)^{-\frac{1}{2}} (2 \ \bar{1} \ \bar{1} \ 2 \ \bar{1} \ \bar{1})$	e_{2u}
B'	$\alpha - \beta$	$(4)^{-\frac{1}{2}} (0 \ 1 \ \bar{1} \ 0 \ 1 \ \bar{1})$	e_{2u}
C'	$\alpha - 2\beta$	$(6)^{-\frac{1}{2}} (1 \ \bar{1} \ 1 \ \bar{1} \ 1 \ \bar{1})$	b_{2g}

The symbols at the right under "Symmetry" are taken from the usual group theoretical notation whereas the symbols to the left under "Level" represent a notation in frequent use in the literature of alternant systems. For a general alternant the occupied molecular orbitals are labelled A, B ... going toward larger negative energies from the energy zero; the unoccupied molecular orbitals A', B' ... are symmetrically located on the positive side of the zero of energy and any pair K and K' differ by a sign change in the coefficients of one set of atomic orbitals. The same notation can be used for the substituted alternant if we agree that K will mean that orbital which goes over into K' of the parent hydrocarbon, as the substituents regarded as perturbation are removed. This convention does not imply that ... B, A, A', B' ... be in ascending energy order as they are in the unsubstituted case. We shall use this notation later when we give diagrams of the energy levels of the substituted ring and we shall see that two levels, as a function of the perturbation, can actually cross.

a) Mono-substituted benzene ring.

If we consider a perturbation matrix V with a single non-zero element, say V_{11} , we have from equation (28),

$$c_1 = -\frac{1}{F_v(a)} \sum_{k=0}^v (-1)^k \epsilon_k \mathcal{L}_{v-k}(a) [V_{(1+k)',1} + V_{(1-k)',1}] c_1 \quad (50)$$

From this we obtain, on carrying out the summation

$$c_1 = -\frac{1}{F_v(a)} \epsilon_0 \mathcal{L}_v(a) [V_{1,1} + V_{1,1}] c_1 \quad (51)$$

or

$$V_{11} = -\frac{F_v(a)}{\mathcal{L}_v(a)} = -\frac{\mathcal{L}_{v+1}(a) - \mathcal{L}_{v-1}(a)}{\mathcal{L}_v(a)} \quad (52)$$

It is possible, of course, to write the \mathcal{L}'_s out explicitly so that we have an implicit equation for the energy parameter a in terms of the perturbation matrix elements. Thus far, we have found it more practical and instructive in the cases we have dealt with, to use tables of Chebyshev polynomials directly and calculate V_{11} for a number of different values of a . The energy E can then be graphically displayed as a function of V .

Let us consider, for example, a six membered unperturbed benzene ring. The substitution of a nitrogen atom for a carbon and hydrogen atom

pair gives pyridine as our perturbed system and equation (52) becomes

$$V_{11} = - \frac{F_3(a)}{\mathcal{L}_3(a)} = - \frac{\mathcal{L}_1(a) - \mathcal{L}_2(a)}{\mathcal{L}_3(a)} \quad (53)$$

It is a matter of a short time to find the behaviour of all of the energy levels as a function of the strength of the perturbation. We show this behaviour in Figure 1. We see that two of the energy levels of benzene remain unperturbed by a single diagonal perturbation. This is to be expected since there are two molecular orbitals in the Hückel theory of benzene for which the coefficients of the atomic orbital centred on the site of the localized perturbation vanish and overlap and inductive effects have been neglected.

The asymptotes for the energy levels can be found simply by putting the denominator equal to zero in equation (53), that is to say, the roots of $\mathcal{L}_3(a) = 0$ are the asymptotes provided, of course, that they are not also roots of the numerator. In the limit of very large perturbations, the levels which split off are given by $V(a) = a$. A more general discussion of this effect has been given by Löwdin in reference 1. It is interesting to observe that if $V_{11} = 0$ we have $F_3 = 0$ which gives the energy levels of the unperturbed problem. Thus we can always write F_v in factorized form since we will always know the unperturbed energy levels, e.g.

$$F_3 = (a+1)(a-1)(a+2)(a-2) \quad (54)$$

It is also interesting to note that the energy levels split off from the top and bottom of the "band" just as in the case of localized perturbations in solids⁴⁹⁾. We shall see later that we have one level splitting for each substituted atom. We also observe that the energy levels which are perturbed all move in the same direction.

49) See the discussions in references 42 and 43.

The eigenvectors of the perturbed system can be found from equation (28). Thus, we find for C_2

$$C_2 = - \frac{1}{F_3} \sum_{k=0}^2 (-1)^k \epsilon_k \mathcal{L}_{v-k} \left[V_{(2+k)',1} + V_{(2-k)',1} \right] C_1 = \frac{\mathcal{L}_2 V_{11} C_1}{F_3} \quad (55)$$

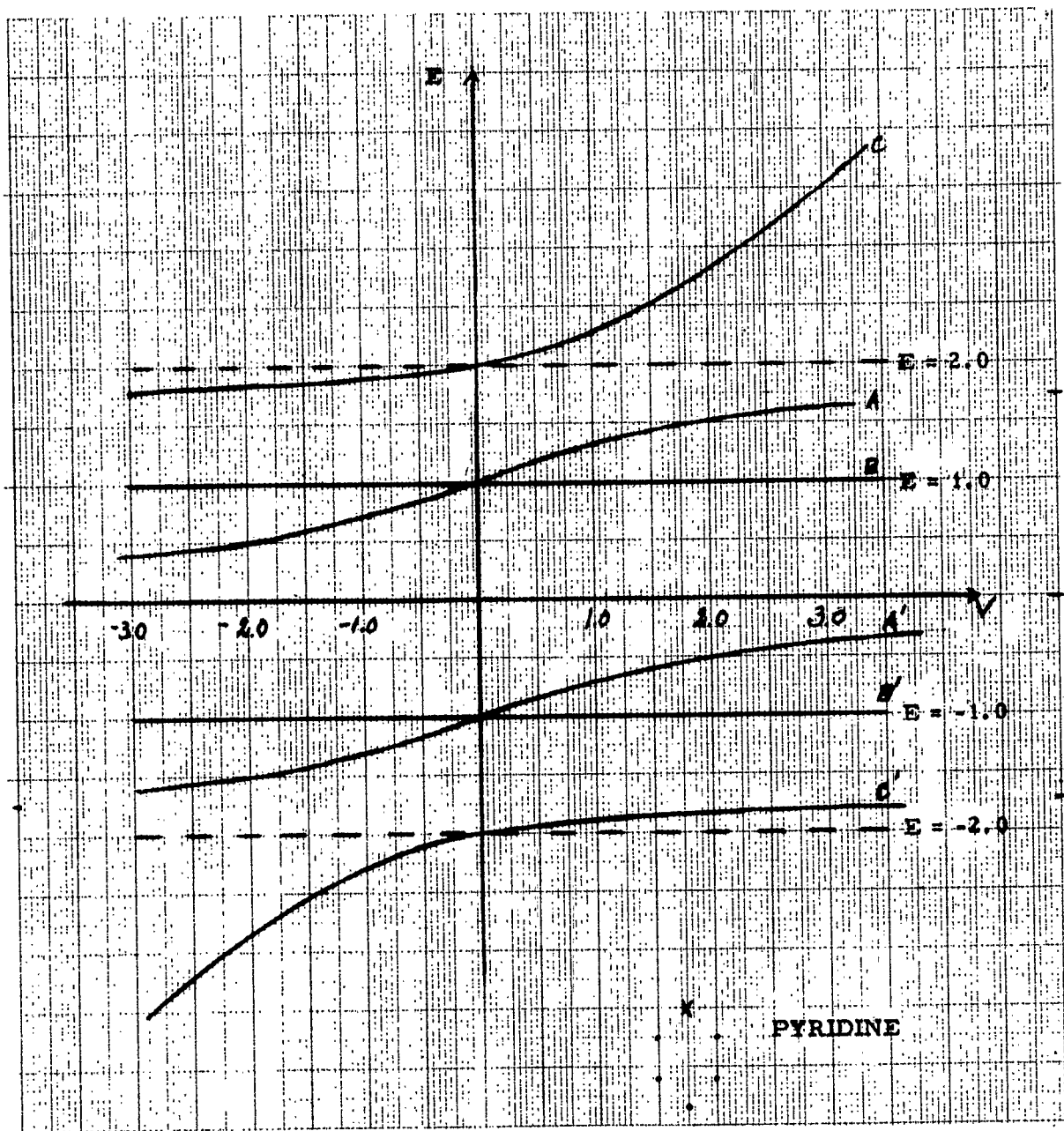


Figure 1. The energy levels of pyridine as a function of the strength of a single diagonal perturbation. Side markers indicate the asymptotes. A, A' etc. label the symmetry levels as discussed in the text for benzene.

But from equation (53),

$$\frac{V_{11}}{F_3} = -\tau_3^{-1} \quad (56)$$

so that

$$c_2 = -\tau_2 \tau_3^{-1} c_1 \quad (57)$$

In a similar way, we find that

$$c_3 = \tau_1 \tau_3^{-1} c_1 \quad (58)$$

$$c_4 = -\tau_4 \tau_3^{-1} c_1 \quad (59)$$

$$c_5 = c_3 \quad \text{and} \quad c_6 = c_2 \quad (60)$$

Of course, we know already the eigenvectors going with the unperturbed levels.

To find the eigenvectors corresponding to any value of the perturbation V_{11} , it is only necessary to use Figure 1 to pick out the corresponding eigenvalue, turn to the tables of Chebyshev Polynomials, tabulate the τ 's and carry out the operations indicated. The calculation of eigenvectors for any value of V_{11} can be carried out quickly, for this case and the accuracy is limited only by the accuracy with which the eigenvalue can be read from the graph and by the accuracy with which the polynomials are tabulated (3 decimal places in the tables cited in reference 45 with an interpolation scheme if more figures are needed). For future reference, we give the matrix \mathcal{C} for the mono-substituted benzene ring when $V_{11} = 1$

$$\mathcal{C} = \begin{bmatrix} 0.646 & 0.517 & 0.000 & 0.497 & 0.000 & 0.262 \\ 0.413 & 0.082 & 0.500 & -0.423 & 0.500 & -0.379 \\ 0.295 & -0.409 & 0.500 & -0.198 & -0.500 & 0.455 \\ 0.259 & -0.621 & 0.000 & 0.563 & 0.000 & -0.481 \\ 0.295 & -0.409 & -0.500 & -0.198 & 0.500 & 0.455 \\ 0.413 & 0.082 & -0.500 & -0.423 & -0.500 & -0.379 \end{bmatrix} \quad (61)$$

Once \mathcal{C} is known, the first order density matrix given by equation (3) can be calculated readily and since we also may wish to have it for

reference in later work we give it here:

$$\rho = \begin{bmatrix} 0.685 & 0.310 & -0.020 & -0.154 & -0.020 & 0.310 \\ 0.310 & 0.427 & 0.338 & 0.056 & -0.162 & -0.072 \\ -0.020 & 0.338 & 0.504 & 0.330 & 0.004 & -0.162 \\ -0.154 & 0.056 & 0.330 & 0.453 & 0.330 & 0.056 \\ -0.020 & -0.162 & 0.004 & 0.330 & 0.504 & 0.338 \\ 0.310 & -0.072 & 0.162 & 0.056 & 0.338 & 0.427 \end{bmatrix} \quad (62)$$

b) Di-substituted benzene ring.

Here, we consider the case that the perturbation matrix V has two non-zero elements (assumed equal), both located on the diagonal. From equation (28), two relationships among the C 's can be obtained and the solution of these gives an expression for the strength of the perturbation in terms of Chebyshev polynomials of the energy parameter. Also the eigenvectors and hence the density matrix can be readily obtained from equation (28). The procedure is exactly the same as in the mono-substituted case except that now there are two equations instead of one to solve so that the calculation is somewhat more involved but still quite simple.

For the six membered ring there are three distinct possibilities for the position of the two heteroatoms. These are shown in the following diagrams with the corresponding equation for V and the eigenvectors (unnormalized).

PYRIDAZINE



$$V = - \frac{F_3}{\tau_3 \mp \tau_2} \quad (63)$$

$$c_2 = \pm c_1; \quad c_3 = \frac{\tau_1 \mp \tau_2}{\tau_3 \mp \tau_2} c_1 = \pm c_6; \quad c_4 = \frac{\tau_1 \mp \tau_2}{\tau_3 \mp \tau_2} c_1 = \pm c_5 \quad (64)$$

PYRIMIDINE

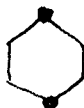


$$V = - \frac{F_3}{\tau_3 \mp \tau_1} \quad (65)$$

$$c_1^- = 0; \quad c_2^- = c_6^-; \quad c_3^- = \frac{1}{\tau_1} c_6^-; \quad c_4^- = 0; \quad c_5^- = -c_3^- \quad (66)$$

$$c_1^+ = -\frac{\tau_2}{\tau_1} c_6^+; \quad c_2^+ = c_6^+; \quad c_3^+ = -\frac{\tau_1}{\tau_2} c_6^+; \quad c_4^+ = \frac{\tau_2}{\tau_1} c_6^+; \quad c_5^+ = c_3^+ \quad (67)$$

PYRAZINE



$$V = - \frac{F_3}{\tau_3 \mp \tau_0} \quad (68)$$

$$c_2 = \frac{-\tau_2 \pm \tau_1}{\tau_3 \mp \tau_0} \quad c_1 = \pm c_3 = \pm c_5 = \mp c_6 \quad ; \quad c_4 = \pm c_1 \quad (69)$$

The simplicity of these equations is such that it is possible to obtain $E = E(V)$ curves in a short time. Care must be taken, however, to associate the eigenvalues and eigenvectors correctly. In the above equations, the top sign in the denominator of the energy expression always must be associated with the top sign in the expression for the coefficients. For pyrimidine we have introduced an obvious notation which can be used in lieu of the above convention when necessary. It may seem curious, that, in each of the above cases, we have two expressions for V each apparently of the fourth degree and therefore we should expect eight energy levels altogether. If we were to write the denominators and numerators out in terms of the a 's we would find that in all cases just enough roots of the unperturbed problem are contained in the denominator to cancel the corresponding roots in the factored form of the numerator and thus reduce the degree of the equations. For example we have for pyridazine in terms of a

$$V(a) = - \frac{(a+1)(a-1)(a+2)(a-2)}{(a-2)(a^2+a-1)} \quad (70)$$

This point is discussed in more detail and for the general case in reference 1.

The $E(V)$ vs V curves for the disubstituted six membered ring are given in Figures 2 - 4. We note that two levels split off from the band in these cases. The eigenvectors and hence the density matrices can be obtained in a straight forward manner.

c) Tri-substituted benzene ring.

For this case we have three diagonal elements in the V matrix. As in the case of the di-substituted ring, there are three distinct possibilities for the positions of the heteroatoms, i.e.



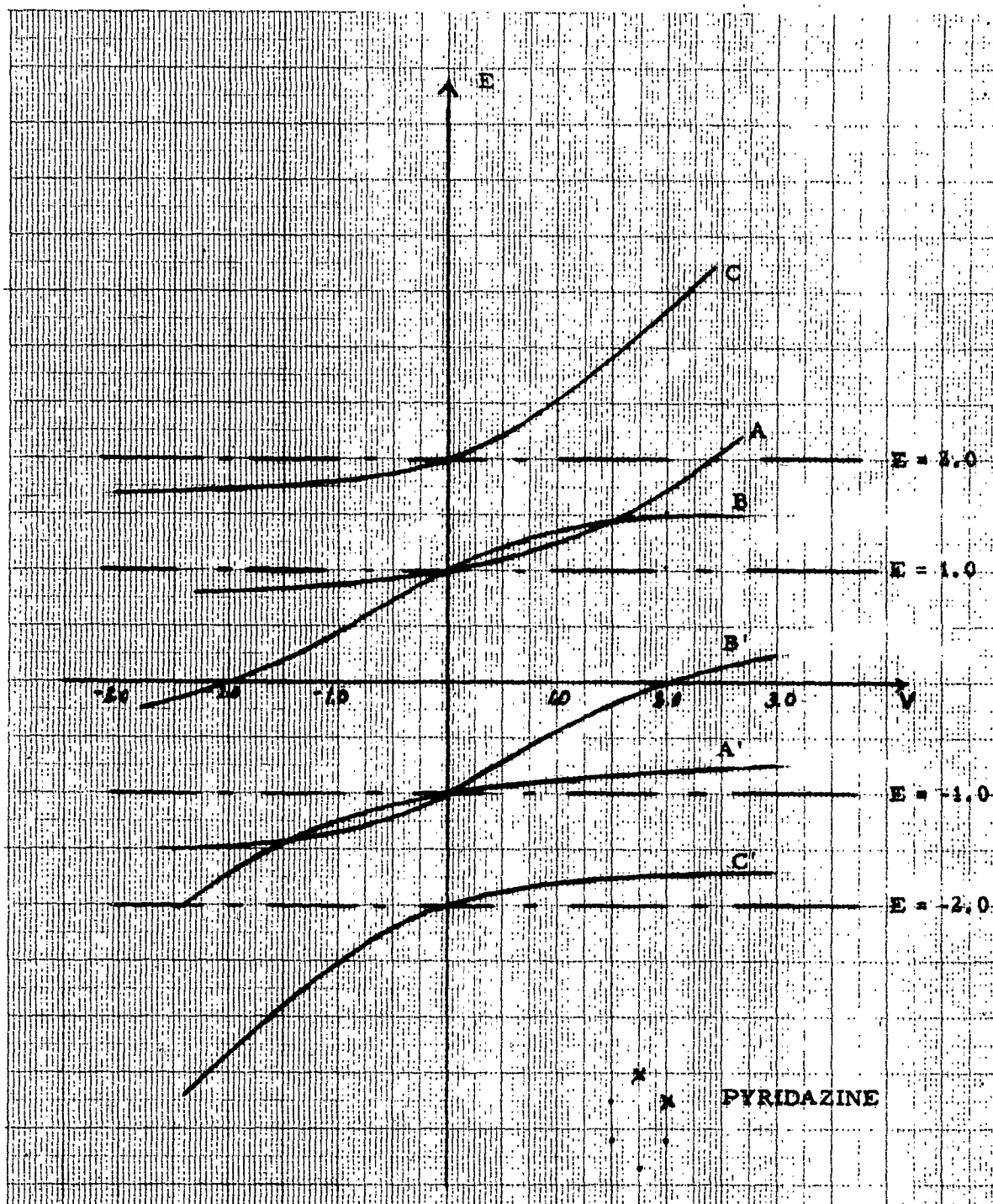


Figure 2. The energy levels of pyridazine as a function of the strength of the perturbation.

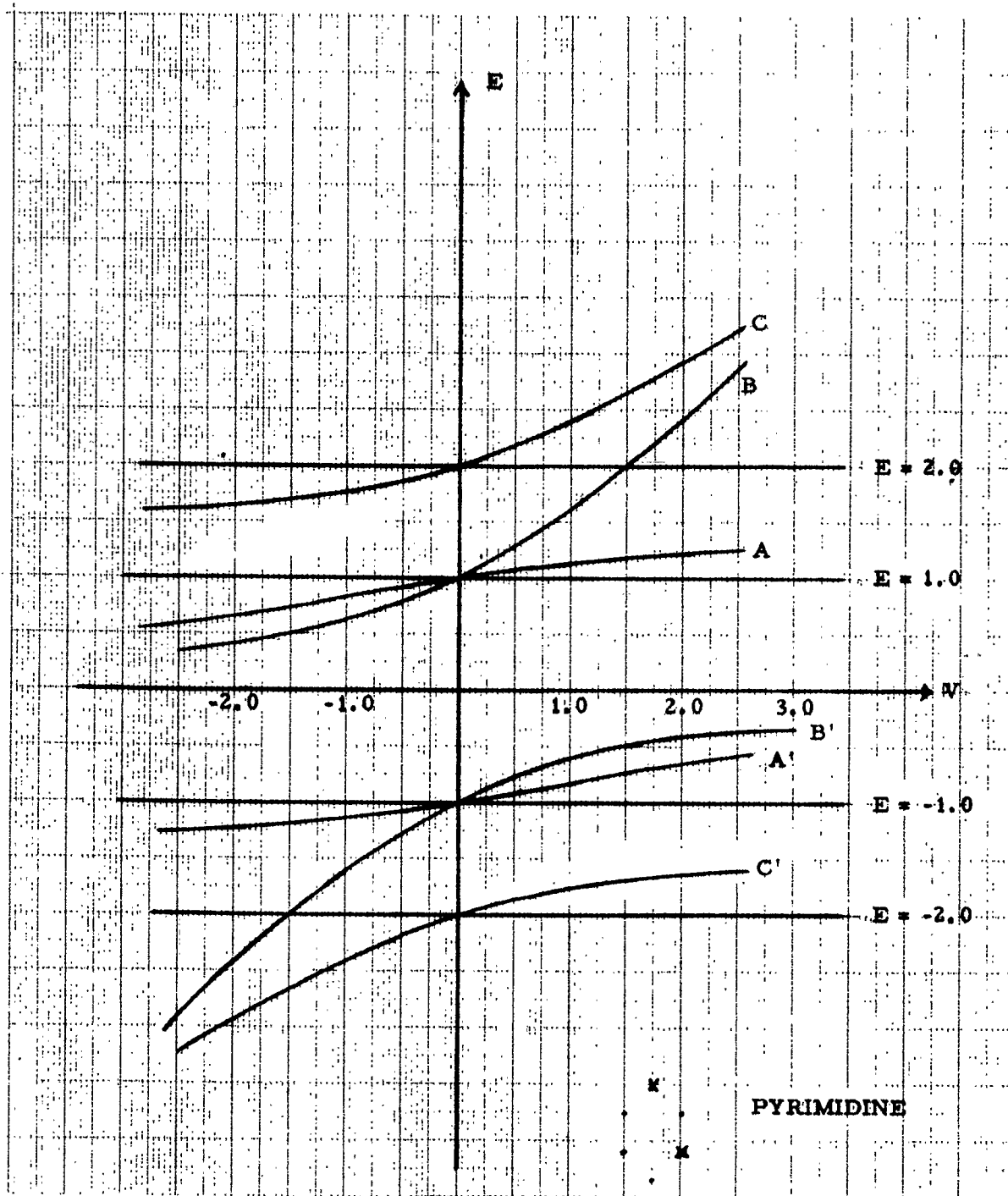


Figure 3. The energy levels of pyrimidine as a function of the strength of the perturbation.

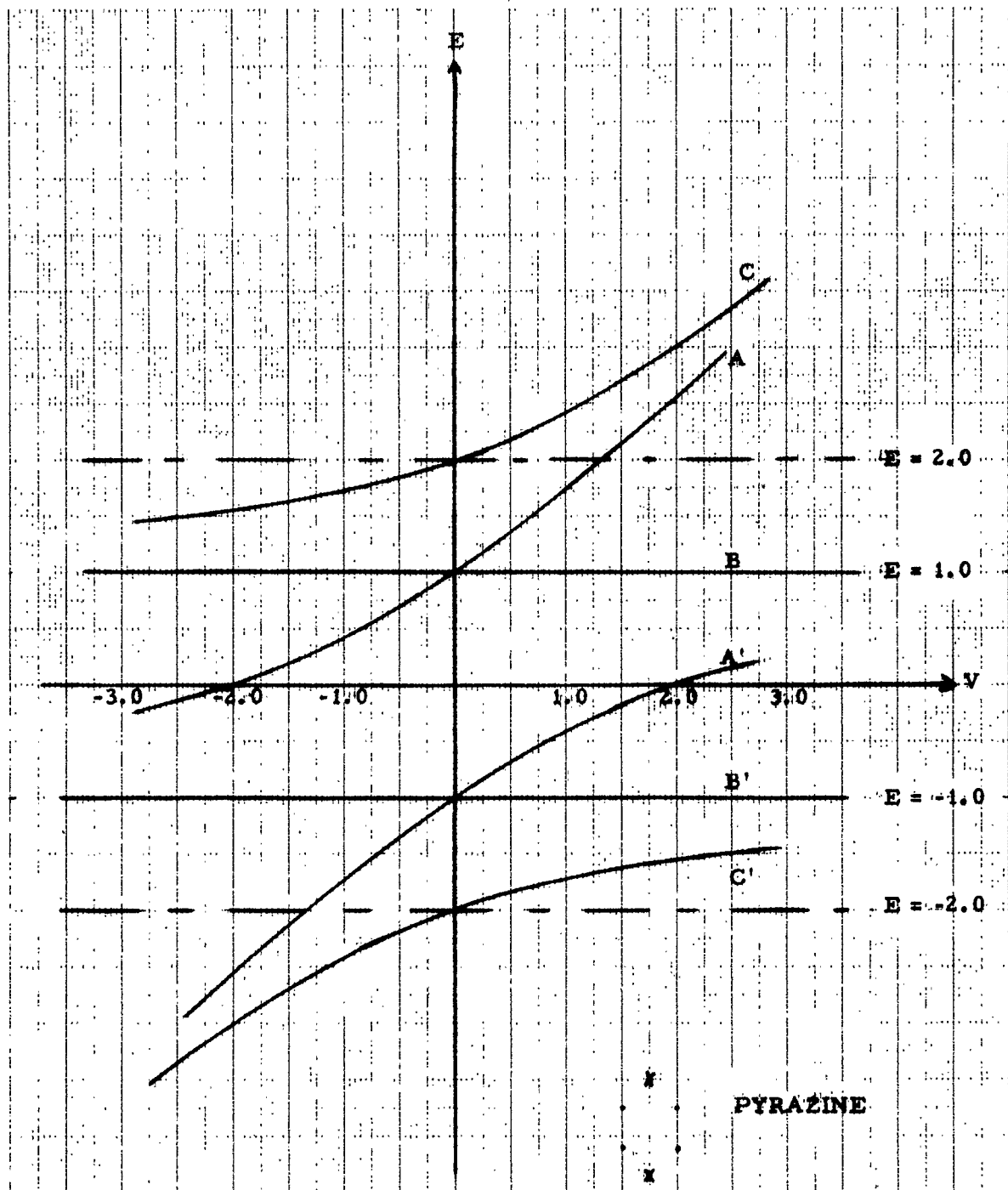


Figure 4. The energy levels of pyrazine as a function of the strength of the perturbation.

We shall consider only the last of these for two reasons: 1) it is the most stable molecule of the three and 2) the symmetry of the molecule makes it easy to solve the equations by our present method. We find that

$$(a) \quad V = -\frac{F_3}{\tau_3 + \tau_0 \tau_1} \quad \text{and} \quad \gamma = -\frac{F_3}{\tau_3 - \tau_1} \quad (71)$$

Here we have two expressions with different terms in the denominator rather than the $+$ signs familiar from the disubstituted cases. Also the second expression here is the same as the expression for V in the case of pyrimidine if we take the minus sign there. This is easy to understand from the symmetry of the molecule and the form of the unperturbed molecular orbitals.

For the eigenvectors we find that for (a) we have

$$c_1 = c_4 = 0; \quad c_3 = -c_5 \quad \text{and} \quad c_6 = c_2 = \frac{\tau_0 - \tau_3}{\tau_3 - \tau_1} c_5 \quad (72)$$

For (b) we have

$$c_3 = c_5 = c_1; \quad c_4 = c_6 = c_2 \quad \text{and} \quad c_2 = -\frac{\tau_0(\tau_2 + 1)}{\tau_3 + \tau_0 \tau_1} c_1 \quad (73)$$

The energy curves are given in Figure 5. We note that three levels split off in this case although two of them remain degenerate.

d) Perturbations on a seven membered ring.

We can derive equations similar to the above for seven and five membered rings. The procedure is so similar that there is no point in discussing it here. For example, with a single diagonal perturbation equation (29) gives

$$V_{11} = \frac{\overline{G}_2(\alpha)}{\overline{D}_2(\alpha)} \quad (74)$$

in close analogy to the result for the six membered ring.

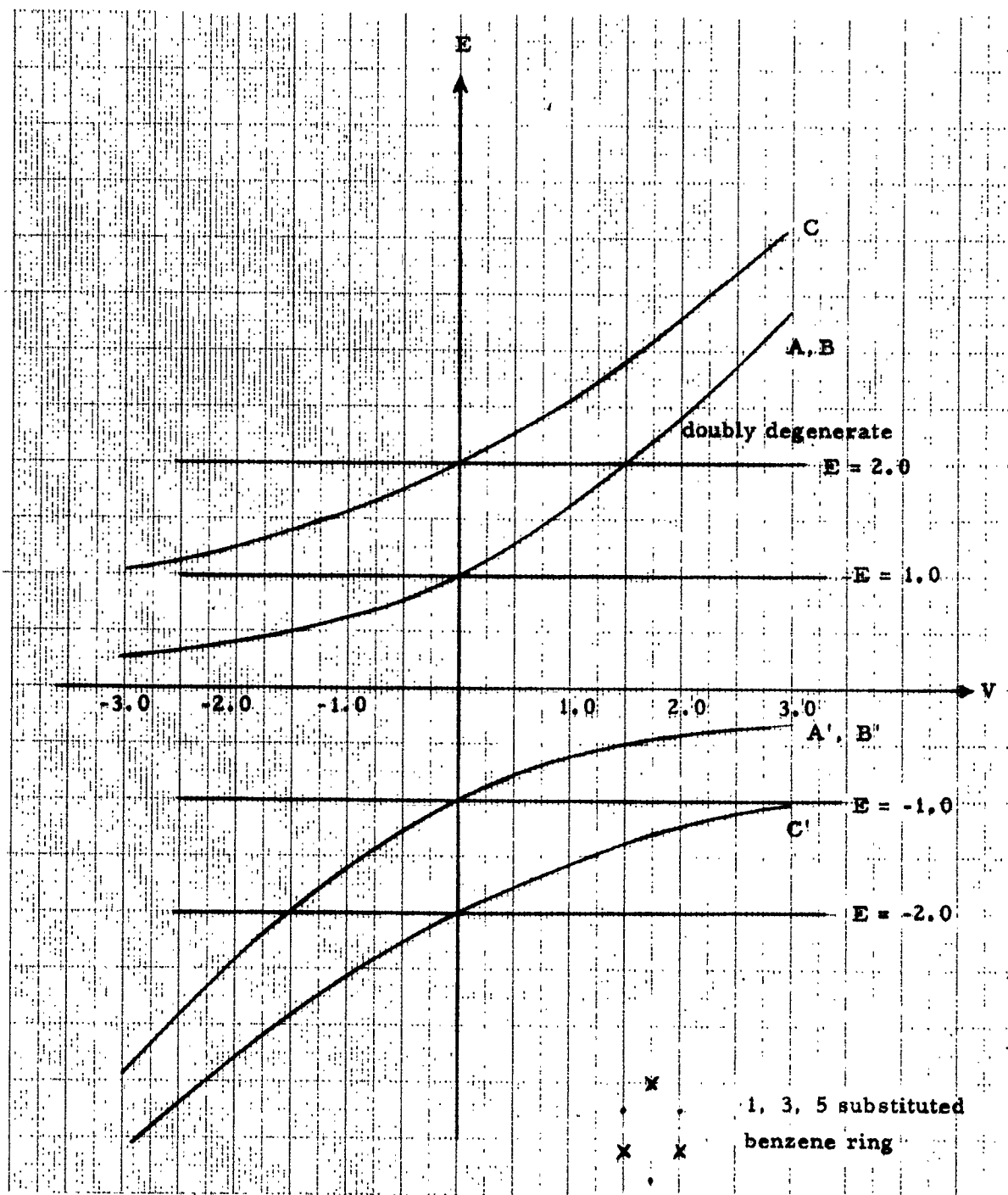
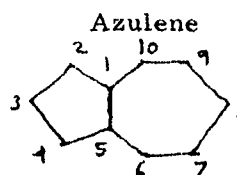
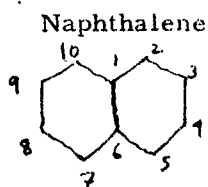


Figure 5. The energy levels of the 1, 3, 5 substituted benzene ring as a function of the strength of the perturbation.

e) Perturbation on a ten membered ring.

Both Naphthalene and Azulene can be considered as perturbed ten membered rings with the perturbation matrix V containing only one non-zero off-diagonal element, $V_{rs} = V_{sr}$ and $V_{rr} = 0$ for all r . (For perturbation to Naphthalene $r = 1$, $s = 6$, and to azulene $r = 1$, $s = 5$, all other $V_{rs} = 0$). Solution of the equation system generated by equation (28) gives the result



$$V_{16} = \frac{\epsilon_6 - \epsilon_4}{\epsilon_6 \pm \epsilon_5} \quad (75)$$

$$V_{15} = \frac{\epsilon_6 - \epsilon_4}{\epsilon_6 \pm \epsilon_5} \quad (76)$$

The $E(V)$ vs V curves and the eigenvectors can be obtained as before but we shall give only the curves for Naphthalene which indicate how complicated the behaviour can be. (Figure 6).

Other applications of this type have been made of the method but it should be clear from these examples that the method is quite useful. We turn next to illustrations of the iterative method.

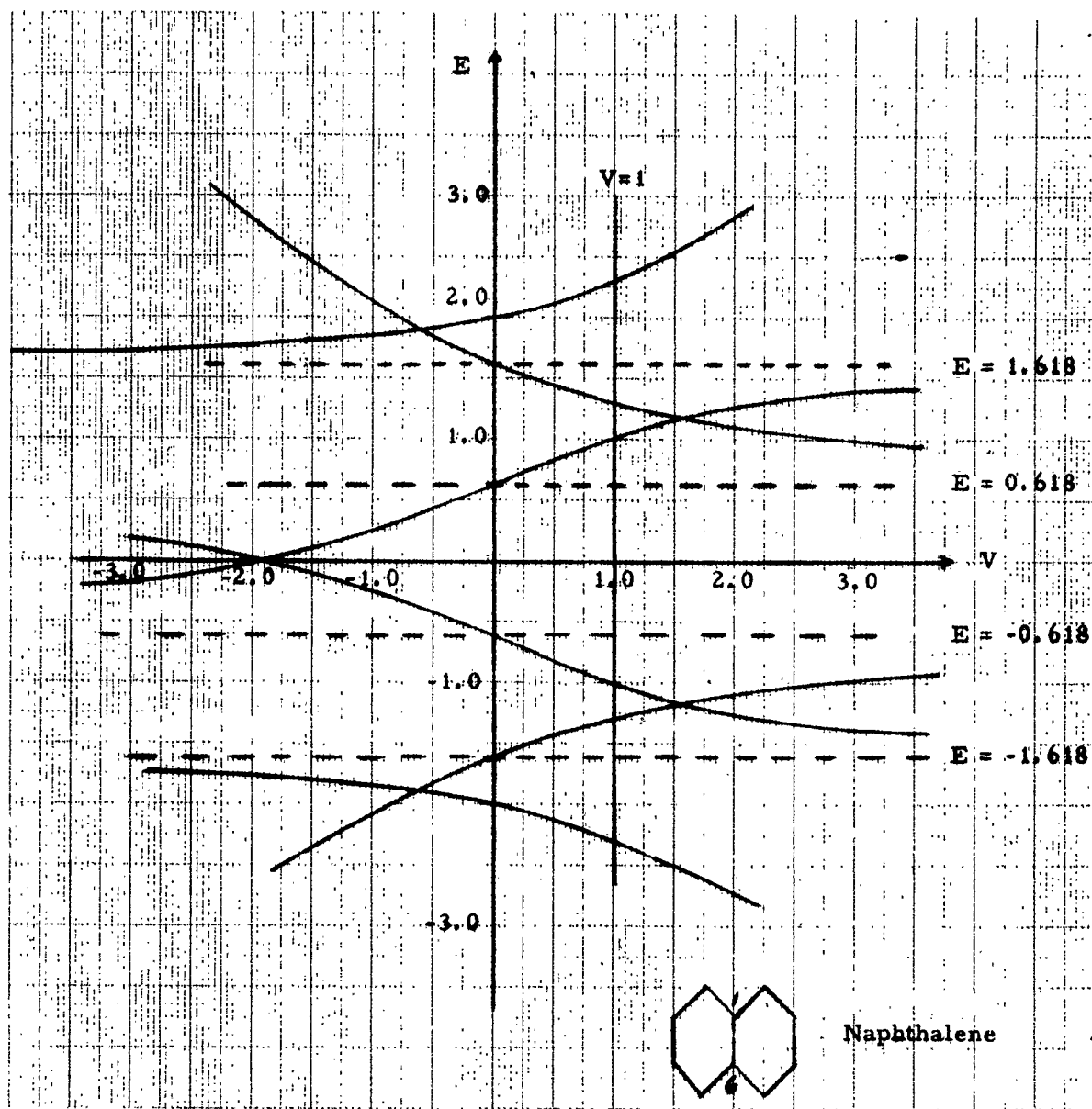


Figure 6. Energy levels of naphthalene as a function of the strength of the 1-6 bond perturbation.

IV. APPLICATIONS OF THE ITERATIVE METHOD

When equation (28) of section II yields more than two equations, or perhaps three if there is a high degree of symmetry in the molecule, it becomes impractical to use the non-iterative method. We shall now illustrate the second or iterative method by showing how the molecules discussed in the tables compiled by Del Re, Mårtensson and Nordling⁵⁰⁾ can be treated.

50) G. Del Re, O. Mårtensson and J. Nordling, Technical Note No. 29 from the Uppsala Quantum Chemistry Group (1959).

In the Hückel theory, as we have seen, using units of β , we can write

$$(21) \quad G \equiv (E\mathbb{1} - H_0)^{-1} = - (M_1 + \alpha\mathbb{1})^{-1}$$

and we know how to obtain this inverse by the method of Chebyshev polynomials. This enables us to solve, by iteration, equation (31) of section II, i.e.

$$(31) \quad NC = (V - VGV)C = 0$$

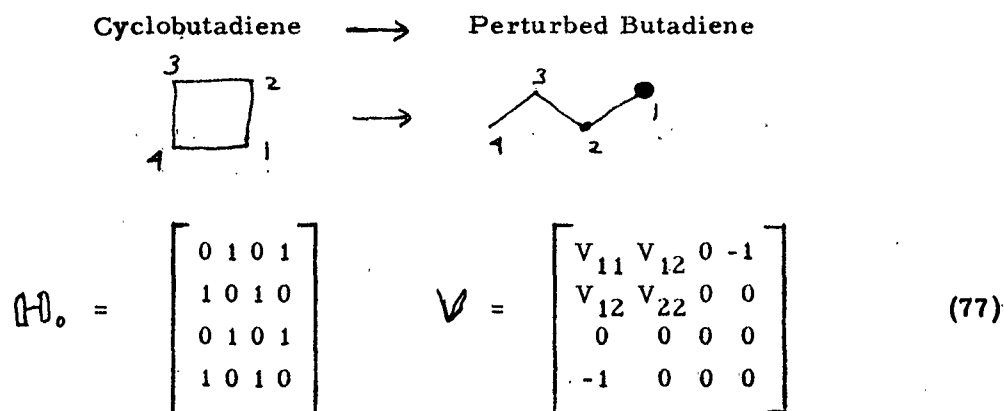
Because of the cyclic character of G only a few elements of the inverse need be computed. We shall list below the quantities needed to carry out the second order iteration procedure for those cases considered in reference 50. These are

- 1) H_0 and V on the basis of Hückel theory,
- 2) $G = (E\mathbb{1} - H_0)^{-1}$ or its first row in terms of Chebyshev polynomials,
- 3) equation (31).

Although these equations, when written out, seem rather cumbersome the actual manipulation of them, though tedious, is not difficult and the convergence of the iterative process is usually quite rapid as we shall indicate by an example. In the figures, the large dots represent large diagonal perturbations and the small dots represent smaller diagonal per-

turbations corresponding to the inductive effect discussed before. In addition to these, there is a bond perturbation connecting the two in all cases.

It should be obvious from the information shown on the following pages that the mathematical structure of all of these problems and many more is quite similar. This is especially clear from the form of the A's and B's which we have defined as an aid in writing the equations in an orderly form.



The -1 in the V_{14} and V_{41} positions breaks the ring.

$$G_{11} = -\mathcal{C}_2 F_2^{-1}; \quad G_{12} = \mathcal{C}_1 F_2^{-1}; \quad G_{13} = -\mathcal{C}_0 F_2^{-1}; \quad G_{14} = \mathcal{C}_1 F_2^{-1} \quad (78)$$

$$\begin{aligned} A_1 C_1 + A_2 C_2 + A_3 C_4 &= 0 \\ A_2 C_1 + A_4 C_2 + A_5 C_4 &= 0 \\ A_3 C_1 + A_5 C_2 + A_6 C_4 &= 0 \end{aligned} \quad (79)$$

$$A_1 \equiv V_{11} - (V_{11}^2 + V_{12} + 1)G_{11} - 2(V_{11}V_{12} - V_{11})G_{12} + 2V_{12}G_{13} \quad (80a)$$

$$A_2 \equiv V_{12} - (V_{11} + V_{22})V_{12}G_{11} - (V_{11}V_{22} + V_{12}^2 - V_{12})G_{12} + V_{22}G_{13} \quad (80b)$$

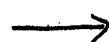
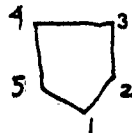
$$A_3 \equiv -1 + V_{11}G_{11} + (V_{12} - 1)G_{12} \quad (80c)$$

$$A_4 \equiv V_{22} - (V_{12}^2 + V_{22}^2)G_{11} - 2V_{12}V_{22}G_{12} \quad (80d)$$

$$A_5 \equiv V_{12}G_{11} + V_{22}G_{12} \quad (80e)$$

$$A_6 \equiv -G_{11} \quad (80f)$$

Cyclopenta-dienyl
radical



Pentadienyl radical



$$H_0 = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 \end{bmatrix} \quad V = \begin{bmatrix} V_{11} & V_{12} & 0 & 0 & -1 \\ V_{12} & V_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (81)$$

$$G_{11} = \frac{-\mathcal{J}_4}{\mathcal{J}_5 - \mathcal{J}_3 + 2} ; \quad G_{12} = \frac{\mathcal{J}_3 - \mathcal{J}_5}{\mathcal{J}_5 - \mathcal{J}_3 + 2}$$

$$G_{13} = \frac{\mathcal{J}_1 - \mathcal{J}_2}{\mathcal{J}_5 - \mathcal{J}_3 + 2} ; \quad G_{14} = G_{13} ; \quad G_{15} = G_{12} \quad (82)$$

$$A_1 C_1 + A_2 C_2 + A_3 C_5 = 0$$

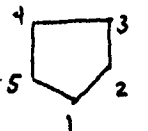
$$A_2 C_1 + A_4 C_2 + A_5 C_5 = 0$$

$$A_3 C_1 + A_5 C_2 + A_6 C_5 = 0$$

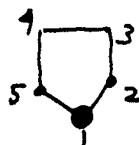
(83)

Note that although the expressions for the A's are the same as in the preceding case the matrix elements of G are different and are given here in terms of the Chebyshev polynomials of the second kind.

Cyclopenta-dienyl
radical



Perturbed form of the radical



H_0 same as in the
previous case.

$$V = \begin{bmatrix} V_{11} & V_{12} & 0 & 0 & V_{12} \\ V_{12} & V_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ V_{12} & 0 & 0 & 0 & V_{22} \end{bmatrix} \quad (84)$$

Note that $V_{15} = V_{12}$ and $V_{55} = V_{22}$ from symmetry. G has been given in the preceding example

$$\begin{aligned} B_1 C_1 + B_2 C_2 + B_3 C_5 &= 0 \\ B_2 C_1 + B_4 C_2 + B_5 C_5 &= 0 \\ B_3 C_1 + B_5 C_2 + B_6 C_5 &= 0 \end{aligned} \quad (85)$$

$$B_1 \equiv V_{11} - (V_{11}^2 + 2V_{12}^2)G_{11} - 4V_{11}V_{12}G_{12} - 2V_{12}^2G_{13} \quad (86a)$$

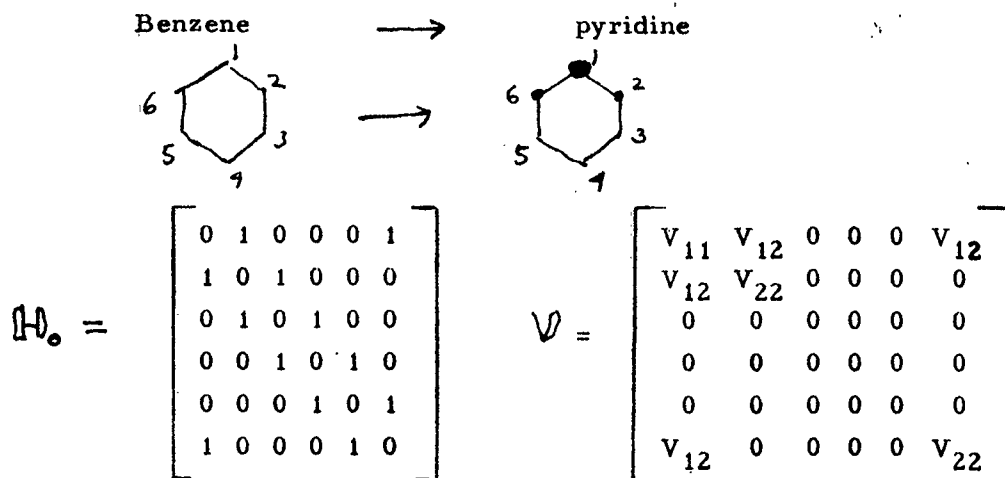
$$B_2 \equiv V_{12} - (V_{11}V_{12} + V_{12}V_{22})G_{11} - (V_{11}V_{22} + 2V_{12}^2)G_{12} - V_{12}V_{22}G_{13} \quad (86b)$$

$$B_3 = B_2 \quad (86c)$$

$$B_4 \equiv V_{22} - (V_{12}^2 + V_{22}^2)G_{11} - 2V_{12}V_{22}G_{12} \quad (86d)$$

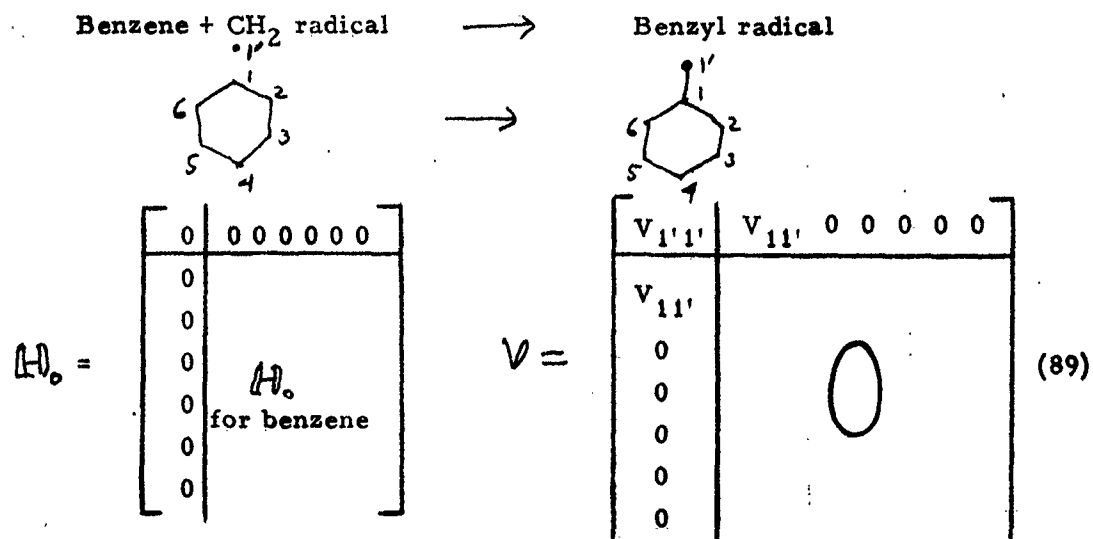
$$B_5 \equiv -V_{12}^2G_{11} - 2V_{12}V_{22}G_{12} - V_{22}^2G_{13} \quad (86e)$$

$$B_6 = B_4 \quad (86f)$$



$$\begin{aligned} G_{11} &= -\mathcal{C}_3 F_3^{-1}; & G_{12} &= \mathcal{C}_2 F_3^{-1}; & G_{13} &= -\mathcal{C}_1 F_3^{-1} \\ G_{14} &= \mathcal{C}_6 F_3^{-1}; & G_{15} &= G_{13}; & G_{16} &= G_{12} \\ F_3 &= \mathcal{C}_4 - \mathcal{C}_2 \end{aligned} \quad (87)$$

$$\begin{aligned} B_1 C_1 + B_2 C_2 + B_3 C_6 &= 0 \\ B_2 C_1 + B_4 C_2 + B_5 C_6 &= 0 \\ B_3 C_1 + B_5 C_2 + B_6 C_6 &= 0 \end{aligned} \quad (88)$$



$$G_{\alpha\alpha} = -\mathcal{E}_1^{-1} ; \quad G_{1\alpha} = G_{\alpha 1} = 0 \quad \text{for } \alpha = 1, \dots, 6 \quad (90)$$

G_{11} , G_{12} etc. are the same as for benzene

$$\begin{aligned} D_1 c_1' + D_2 c_1 &= 0 \\ D_2 c_1' + D_3 c_1 &= 0 \end{aligned} \quad (91)$$

$$D_1 \equiv V_{1'1'} - V_{1'1'}^2 G_{1'1'} - V_{11'}^2 G_{11} \quad (92a)$$

$$D_2 \equiv V_{11'} - V_{11'} V_{11'} G_{11} - V_{1'1'} V_{11'} G_{1'1'} \quad (92b)$$

$$D_3 \equiv V_{11} - V_{11}^2 G_{11} - V_{11'} G_{1'1'} \quad (92c)$$

To demonstrate the use of the above equations and to indicate the speed of convergence of the method, we give now the details of a calculation on a perturbed buta-diene-like system.

We take $V_{11} = 2$, $V_{22} = 0.2$, $V_{12} = 0.3$ and obtain

$$\begin{aligned} A_1 &= 2 - 5.3 G_{11} + 2.8 G_{12} + 0.6 G_{13} \\ A_2 &= 0.3 - 0.66 G_{11} - 0.19 G_{12} + 0.2 G_{13} \\ A_3 &= -1 + 2 G_{11} - 0.7 G_{12} \\ A_4 &= 0.2 - 0.13 G_{11} - 0.12 G_{12} \\ A_5 &= 0.3 G_{11} + 0.2 G_{12} \\ A_6 &= -G_{11} \end{aligned}$$

A starting value, E_0 , of E is chosen, the G 's obtained and the A 's calculated. Any two of the equations in (79) are chosen, C_1 is set equal to unity and C_2 and C_4 are found. We obtained the following results for one of the energy levels of this problem.

TABLE II. Convergence of the iteration process for a perturbed butadiene-like system.

Iteration	E_0	C_0	$d \equiv G_0 V C_0$	E^* (eq. 49)
First	3.0000	1.0000	1.0000	2.77
		0.5359	0.5361	
		-	0.2009	
		-0.2361	0.0669	
Second	2.77	1.0000	1.0000	2.7798
		0.6031	0.6033	
		-	0.2504	
		0.1046	0.0905	
Third	2.7798	1.0000	1.0000	2.77996
		0.600021	0.600021	
		-	0.247936	
		0.089418	0.089192	
Fourth	2.77996	1.00000	0.999999	2.779963
		0.599931	0.599958	
		-	0.247890	
		0.089180	0.089165	

We see from this table that the convergence is quite rapid and indeed the second iteration would suffice for most purposes. For all of the examples which we have worked out the second or third iteration has given us the accuracy we needed. Of course, the number of iterations required depends on the accuracy of the initial energy guess E_0 which of necessity should be chosen different from the unperturbed eigenvalues, but in most

cases one has a rather good idea of what this should be. It should be mentioned here that if any of the eigenvectors of the perturbed problem has $C_1 = 0$, then that eigenvalue and eigenvector cannot be obtained by this second order iteration procedure. Since one is dealing with finite matrices, one could find out which eigenvalues are lost (excluding those which are unperturbed) and apply alternative partitioning procedure to get these by similar procedures.

V. DISCUSSION

We have attempted in this report, to indicate how the methods described in reference 1 can be applied to problems of chemical and physical interest. Here we wish to give a brief discussion of the relative merits of the two methods and to point out some possible areas for application of them.

First, we recognize that the two methods are basically the same; the iterative method is introduced only when the complexity of the perturbation matrix V becomes too great to make the first method tractable. Hence the iterative method, though rather complex, is much more flexible and powerful than the non-iterative method. The usefulness of the non-iterative method can be extended somewhat by going to first order perturbation theory as we shall now indicate.

Let us assume that the Hamiltonian matrix of our problem can be written as

$$H = H_0 + V_0 + V' \quad (93)$$

where H_0 is the matrix of the basic, unperturbed problem, e.g. benzene,

V_0 is a large perturbation corresponding to one of the problems solved in Section III and V' is a small perturbation matrix representing diagonal and/or off-diagonal perturbations on the substituted ring problem whose matrix is $H_0 + V_0$, then from first order perturbation theory we have that

$$E' = C^+ V' C. \quad (94)$$

We have already solved the eigenvalue problem corresponding to $H_0 + V_0$.

for a number of useful cases so that by a single first order perturbation correction we can extend our results considerably.

As an example, we consider pyridine with both inductive effects and bond perturbations. We take $V'_{12} = V'_{16} = 0.3$ and $V'_{22} = V'_{66} = 0.1$ in the perturbation matrix V' and $V_{11} = 1$ in the matrix V_0 with all other elements in both matrices equal to zero. We used the iterative method to find out the exact eigenvalue to the accuracy we needed and in Table III we compare the results obtained by the iterative and the non-iterative perturbation method. Since the bond perturbation is rather large, we expect that most of the error in E_p , the perturbation value, is introduced by it and, therefore, we also show the results of the two methods when $V'_{12}V'_{16} = 0$ but $V'_{22} = 0.1$ i.e. inclusion of a purely inductive effect.

TABLE III. Comparison of the first order perturbation results E_p with the exact results obtained by the iterative method, E_I , for pyridine.

Energy level	$V'_{12} = 0.3 ; V'_{22} = 0.1$		$V'_{12} = 0 ; V'_{22} = 0.1$	
	E_p	E_I	E_p	E_I
C	2.633	2.6601	2.3125	2.3132
B	1.370	1.3550	1.3187	1.3188
A	1.050	1.0512	1.0500	1.0512
A'	-0.921	-0.9057	-0.6688	-0.6684
B'	-0.950	-0.9512	-0.9500	-0.9512
C'	-1.982	-2.0094	-1.8625	-1.8636

It is obvious from this table that an inductive effect of the magnitude considered here can be included by first order perturbation theory with sufficient accuracy and even inclusion of the bond perturbation in this way may be adequate for many purposes. In any case, it is possible to consider the first order perturbation energy as a zeroth approximation in the

iterative method.

The first order perturbation approach should be quite useful in all of those problems where there are a number of large diagonal perturbations which are almost but not necessarily exactly equal and other small diagonal or off-diagonal perturbations. Many compounds and series of compounds of biochemical interest should fall into this category.

The non-iterative method, because it gives a closed analytical form for the $E = E(V)$ or more exactly $V = V(E)$, relationship, is useful for discussing and obtaining insight into those properties of simple, cyclic systems which are principally determined by a few large, localized perturbations. The details introduced by small perturbations can then be accounted for as minor corrections. The iterative method, on the other hand, can be programmed for a computer and its value will be particularly evident when a series of calculations on related systems must be carried out with high accuracy. It should be kept in mind that the equation $NC = 0$ reduces the magnitude of any problem considerably because the number of non-vanishing elements in V becomes the measure of the "size" of the problem.

In all of our calculations and discussions we have neglected the effects introduced by overlap of basic atomic orbital set. This is physically unrealistic. The second order iteration procedure can be extended easily for the case including overlap. Further study is in progress on this aspect of the problem. (See Appendix II).

Turning now to the applications of these methods we can mention several possibilities.

a) Further applications to conjugated, aromatic systems.

Besides the many possibilities which exist for perturbation on the basic benzene ring, there are similar applications to five and seven membered rings. In Section III, we showed how Naphthalene and azulene can be treated as perturbed (crosslinked) ten membered ring and we have treated the same molecules with substituents at selected points. It should eventually be possible to treat many more cross-linked chains by these methods.

The application of the method to molecules of biochemical importance should be quite profitable. Even the very simple quantities obtained for

these molecules by Hückel theory such as the energies of the highest occupied molecular orbital (HOMO) and the lowest empty molecular orbital (LEMO) have been of great value in obtaining insight into the electronic nature of biochemical processes. Here one is not so much interested in the exact energy values but rather in the variation of the energies among a series of molecules of the same general structure ⁵¹⁾. It is also important to realize that with these methods it is not necessary to calculate all of the energy levels simultaneously as in the case with the usual solution of the secular equation of the problem. One can concentrate attention on the energies of the HOMO and the LEMO and follow their variation with molecular structure and forget about the other energy levels.

51) B. Pullman and A. Pullman, *Revs. Modern Phys.* 32, 428 (1960)

b) One dimensional problems.

The use of one dimensional models as prototypes for three dimensional problems is very common and valuable in physics and chemistry even though three dimensional problems may exhibit effects not occurring in the one dimensional analogues. We consider it quite possible that such problems as the electronic ⁵²⁾ and vibrational ⁵³⁾ properties of a linear chain with impurities, one-dimensional alloys, anti-ferromagnetic linear chain and other one-dimensional order-disorder phenomenon can be treated either exactly or in good approximation with these methods.

52) See reference 42.

53) See reference 43.

c) Three dimensional problems.

The extension of the one-dimensional calculations to two and three dimensions is not trivial although one has an intuitive feeling that the cyclic symmetry which permits the inverse of the corresponding matrix to be found by the method of Chebyshev polynomials can be displayed in three dimensional problems. This will probably be easy in some cases, difficult in others. In any case, we can be certain that in solid state physics, even

the simple calculations which are based on assumptions similar to those made in the Hückel theory of molecules will be needed for some time to come and hence we need not be embarrassed by the crudity of our assumptions.

We have work underway on some of these applications and we shall try to report further on them at a later date.

ACKNOWLEDGMENT

The authors would like to thank Professor P. O. Löwdin for suggesting the problem, stimulating discussions and criticism throughout all stages of the work and for the opportunity of working in the stimulating atmosphere of the Quantum Chemistry Group. Thanks are also due to Dr. L. B. Rédei for some helpful discussions.

APPENDIX I

Chebyshev Polynomials

The Chebyshev polynomials of the first kind are defined by

$$T_n(x) = 2 \cos n\theta = 2 \cos \left(n \arccos \frac{1}{2}x \right)$$

where $x = 2 \cos \theta$.

The polynomials $T_n(x)$ satisfy the following recurrence relation

$$T_{n+1}(x) = x T_n(x) - T_{n-1}(x)$$

The polynomials of any arbitrary degree n can be generated by the above recurrence relation with the starting values $T_0(x) = 2$; $T_1(x) = x$.

The Chebyshev polynomials of the second kind are defined by

$$U_n(x) = \frac{\sin (n+1)\theta}{\sin \theta} = \frac{2 \sin \left[(n+1) \arccos \frac{1}{2}x \right]}{\sqrt{4-x^2}}$$

where $x = 2 \cos \theta$.

The polynomials $U_n(x)$ satisfy the recurrence relation

$$U_n(x) = x U_{n-1}(x) - U_{n-2}(x)$$

with $U_0(x) = 1$ and $U_1(x) = x$.

The relation between $T_n(x)$ and $U_n(x)$ is given by

$$T_n(x) = U_n(x) - U_{n-2}(x)$$

The explicit representations of $U_n(x)$ and $T_n(x)$ in powers of x are

$$\begin{aligned} U_n(x) &= x^n - \binom{n-1}{1} x^{n-2} + \binom{n-2}{2} x^{n-4} - \dots \\ T_n(x) &= x^n - \left[2 \binom{n-1}{1} - \binom{n-2}{1} \right] x^{n-2} + \left[2 \binom{n-2}{2} - \binom{n-3}{2} \right] x^{n-4} - \dots \end{aligned}$$

APPENDIX II

INCLUSION OF OVERLAP

We have

$$(H_0 + V)C = E(1 + S_0 + S)C \quad (A1)$$

where S is the perturbation matrix on S_0 which is the overlap matrix characteristic of the cyclic unperturbed problem,

$$S = S^\dagger \quad (A2)$$

We can write equation (A1) as

$$C = [E(1 + S_0) - H_0]^{-1} (V - ES)C \quad (A3)$$

Define $W(E) = V - ES$; $K = [E(1 + S_0) - H_0]^{-1}$

and note that $W = W^\dagger$

so

$$C = KWC$$

or

$$(1 - KW)C = 0 \quad (A4)$$

The matrix K can be written as

$$K = [E(1 + S_1 M_1 + S_2 M_2 + \dots + S_k M_k) - H_0]^{-1}$$

where S_1 is the overlap integral between nearest neighbours, S_2 between second nearest neighbours and so on. So the matrix K can be inverted in terms of Chebyshev polynomials (Section III of reference 44) and we can apply the non-iterative method or iterative method as before with slight modification.

To apply partitioning technique, we convert the matrix $(1 - KW)$ into a hermetian matrix by premultiplying by W . So we get

$$(W - WKW)C = 0 \quad (A5)$$

Define $M = W - WKW$

$$Mc = 0 \quad (A6)$$

Following the procedure outlined earlier, we construct a second order iteration scheme

$$E^* = E_0 - \frac{[Mc]_1}{c^+ M' c}$$

where the prime denotes differentiation with respect to E . Now

$$M = (V - ES) - (V - ES)K(V - ES) \text{ and}$$

$$M' = -S + SK(V - ES) + (V - ES)KS - (V - ES)K'(V - ES)$$

Now $K = [E(1 + S_0) - H_0]^{-1}$

and $K' = -K(1 + S_0)K$

So

$$M' = -S + SK(V - ES) + (V - ES)KS + (V - ES)K(1 + S_0)K(V - ES).$$

For exact E and C , we have $C = KWC$. But for arbitrary E_0 , $C = C_0$ we have in general

$$d_0 = K_0 W_0 C_0; \quad d_0^+ = C_0^+ W_0 K_0.$$

So

$$c^+ M' c = -c^+ s c_0 + c^+ s d_0 + d_0^+ s c_0 + d_0^+ (1 + s_0) d_0$$

Defining $s c_0 = f_0$, finally we get

$$c^+ M' c = -c^+ f_0 + f_0^+ d_0 + d_0^+ f_0 + d_0^+ (1 + s_0) d_0$$

So the final iteration scheme becomes

$$E^* = E_0 - \frac{[W(c_0 - d_0)]}{-c_0^+ f_0 + f_0^+ d_0 + d_0^+ f_0 + d_0^+ (1 + S) d_0}$$

Following reference 1, we can also consider the non-iterative scheme.

For one diagonal element perturbed, we get from the equation

$$\det \{1 - KW\} = 0,$$

$$1 = K_{11} W_{11}$$

which yields the energy levels E in terms of V_{11} . In a similar way, we can derive an analogous formula for one bond being perturbed only. These equations are slightly more complicated than those in the case of overlap neglected but still simple enough to be quite useful.

RESEARCH REPORTS

List of Technical Notes issued by the Uppsala Quantum Chemistry Group. These Technical Notes are in the United States distributed by "Aeronautical Research Laboratory (RRLC), Wright-Patterson AFB, Ohio". Non-American scientists may obtain copies directly from the Uppsala group.

The mark * indicates that there are no longer any copies available for distribution in Uppsala.

1. Per-Olov Löwdin and Hiroyuku Yoshizumi Correlation Problem in Many-Electron Quantum Mechanics. A survey of the Development and a Discussion of some Current Ideas. June 21, 1957. (Published in Advances in Chemical Physics, ed. I. Prigogine 2, 207, 1959).
2. Per-Olov Löwdin Spin Degeneracy Problem. July 31, 1957. (Published in Coll. Int. Centre Nat. Rech. Sci. 82, 23, Paris 1958)
3. J.O. Hirschfelder and Per-Olov Löwdin The Long-Range Interaction of Two 1s Hydrogen Atoms Expressed in Terms of Natural Spin Orbitals. August 20, 1957. (Published in Molecular Physics 2, 229, 1959).
4. Roberto Fieschi and Per-Olov Löwdin Atomic State Wave Functions Generated by Projection Operators. September 16, 1957.
5. Anders Fröman Calculation of Correlation Energies and Relativistic Corrections of some He- and Ne-like Systems. January 15, 1958. (Published in Phys. Rev. 112, 870, 1958).
6. Per-Olov Löwdin Scaling Problem, Virial Theorem and Connected Relations in Quantum Mechanics. January 20, 1958. (Published in Mol. Spectroscopy 3, 46, 1959).
7. Per-Olov Löwdin Generalization of the Hartree-Fock Scheme. February 20, 1958. (Published in Ann. Acad. Reg. Sci. Upsaliensis 2, 127, 1958).
8. A.J. Freeman and Per-Olov Löwdin On a Quantum Mechanical Kinetic Energy Transformation. March 20, 1958. (Published in Phys. Rev. 111, 1212, 1958).
9. Harrison Shull and Per-Olov Löwdin Variation Theorem for Excited States. April 1, 1958. (Published in Phys. Rev. 110, 1466, 1958).
10. Per-Olov Löwdin and Lajos Rédei Combined Use of the Methods of Superposition of Configurations and Correlation Factor on the Ground States of the Helium-Like Ions. April 15, 1958. (Published in Phys. Rev. 114, 752, 1959).

11. Per-Olov Löwdin An Elementary Iteration-Variation Procedure for Solving the Schrödinger Equation. April 23, 1958.
12. Per-Olov Löwdin Angular Momentum Wave Functions Constructed by Projection Operators. May 10, 1958.
13. Harrison Shull and Per-Olov Löwdin Superposition of Configurations and Natural Spin Orbitals. Applications to the He Problem. June 15, 1958. (Published in J. Chem. Phys. 30, 617, 1959).
14. Per-Olov Löwdin Degeneracies of Atomic dn Configurations Treated by Projection Operator Formalism. July 15, 1958.
- * 15. G.G. Hall Studies on Molecular Crystals. 1. Excitation on a Pure Crystal. August 1, 1958.
- * 16. Proceedings of a panel meeting on "Correspondence between Concepts in Chemistry and Quantum Chemistry" held at Vålådalen, August 26-30, 1958.
- * 17. Harrison Shull The Two-Electron Homopolar Chemical Bond; Hydrogen. September 15, 1958.
- * 18. Report from the Summer School in Quantum Chemistry held in Vålådalen, Sweden, July 26 - August 30, 1958, with summaries of four seminars.
- * 19. H. McIntosh Symmetry-Adapted Functions Belonging to the Symmetric Groups. October 6, 1958. (Published in J. Math. Phys. 1, 453, 1960).
- * 20. G. Del Re On the Non-Orthogonality Problem in the Semi-Empirical MO-LCAO Method. October 20, 1958. (Published in Nuovo Cimento 17, 644, 1960).
- * 21. H. McIntosh Towards a Theory of the Crystallographic Point Groups. November 3, 1958. (Published in J. Mol. Spectroscopy 5, 269, 1960).
- * 22. L. Jansen Symmetry Relations and Electric Multipole Interactions. January 15, 1959.
- * 23. G.G. Hall Studies on Molecular Crystals. 2. Exciton States of Pure Crystals. February 1, 1959.
- * 24. H. Preuss The Idea of Atomic Associations in a Simple Form of Perturbation Method. April 20, 1959.
- * 25. J.L. Calais Derivation of the Clebsch-Gordan-Coefficients by means of Projection Operators. June 1, 1959.

26. Harrison Shull The Nature of the Two-Electron Chemical Bond. I. The Homopolar Case. June 5, 1959. (Published in J. Am. Chem. Soc. 82, 1287, 1960).
27. Per-Olov Löwdin Some Aspects on the Recent Development of the Theory of the Electronic Structure of Atoms. June 1, 1959. (Presented at the second Robert A. Welch Foundation Conference on Chemical Research, II. Atomic Structure. Houston, Texas, December 1-3, 1958).
28. Per-Olov Löwdin Studies in Perturbation Theory. II. Generalization of the Brillouin-Wigner Formalism. III. Solution of the Schrödinger Equation under a Variation of a Parameter. June 15, 1959.
29. Del Re, Mårtensson and Nordling A Numerical Investigation Into Some Aspects of the Semi-Empirical MO-LCAO Method. October 1, 1959.
30. Report from the International Summer Institute in Quantum Chemistry held at Skogshem, Lidingö, in 1959.
31. Z.W. Ritter and R. Pauncz Approximate Analytical Wave Functions for the $1s$ and $1s$ states of He and He-like Ions. October 15, 1959. (Published in J. Chem. Phys. 32, 1820-1825, 1960).
32. J. Linderberg and H. Shull Electronic Correlation Energy in 3- and 4-Electron Atoms. November 1, 1959. (Published in J. Mol. Spectroscopy 5, 1-16, 1960).
33. G.G. Hall Improved Atomic Wave Functions Using a Functional Transformation. November 20, 1959. (Published in Proc. Phys. Soc. LXXV, 575, 1960).
34. A. Fröman Mass Polarization in He-Like Systems. December 1, 1959.
35. P.O. Löwdin Quantum Theory of Electronic Structure of Molecules. January 15, 1960. (Published in Ann. Rev. of Physical Chemistry 11, 107, 1960).
36. P.O. Löwdin Expansion Theorems for the Total Wave Function and Extended Hartree-Fock Schemes. February 15, 1960. (Published in Revs. Modern Phys. 32, 328, 1960).
37. J. de Heer and R. Pauncz Molecular Electronic Integrals for Cyclic Systems. February 15, 1960. (Published in J. Mol. Spectroscopy 5, 326, 1960).
38. A. Fröman Relativistic Corrections in Many-Electron Systems. February 15, 1960. (Published in Revs. Modern Phys. 32, 317, 1960).

39. J.L. Calais and J. Linderberg
Atomic Angular Momentum Wave Functions for the Configurations s^np^m in the Cases of Weak, Strong and Intermediate Coupling. Studied by the Projection Operator Technique. March 1, 1960.
40. J. Linderberg
Exact Perturbation Treatment of Hartree-Fock Equations. March 1, 1960. (Published in Phys. Rev. 121, 816, 1961).
41. Löwdin, Pauncz and de Heer
On the Calculation of the Inverse of the Overlap Matrix in Cyclic Systems. March 15, 1960. (Published in J. Math. Phys. 1, 461, 1960).
42. A. Fröman and G.G. Hall
The Accuracy of Atomic Wave Functions and Their Scale. March 15, 1960. (Published in J. Mol. Spectroscopy 7, 410-423, 1961).
43. T. Arai
Theorem on Separability of Electron Pairs. April 1, 1960. (Published in J. Chem. Phys. 33, 95, 1960).
44. P.O. Löwdin
Note on the Separability Theorem for Electron Pairs. June 15, 1960. (Published in J. Chem. Phys. 35, 78, 1961).
45. T.L. Bailey and J.L. Kinsey
Test of the Conventional Quantum Chemistry Methods on the Hydrogen Atom. July 1, 1960.
46. P.O. Löwdin
Exchange, Correlation and Spin Effects in Molecular and Solid-State Theory. July 15, 1960. (Revs. Modern Phys. 34, 80, 1962).
47. P.O. Löwdin
Studies in Perturbation Theory. IV. Solution of Eigenvalue Problem by Projection Operator Formalism. August 1, 1960. (Accepted for publication in J. Math. Phys.)
48. P.O. Löwdin
----- . V. Some Aspects on the Exact Self-Consistent-Field Theory. August 1, 1960.
49. S.O. Lundqvist
On the Possibility of a Modified Perturbation Scheme for Bound States Involving Discrete Sets Only. August 15, 1960.
50. J.L. Calais and P.O. Löwdin
A Simple Method of Treating Atomic Integrals Containing Functions of r_{12} . September 1, 1960. (Published in J. Mol. Spectroscopy 8, 203-211, 1962).
51. A. Fröman and P.O. Löwdin
Virial Theorem and Cohesive Energies of Solids, Particularly Ionic Crystals. September 15, 1960. (Published in J. Phys. Chem. Solids 23, 75, 1962).
52. J.L. Calais
Nuclear State Wave Functions Generated by Projection Operators. October 1, 1960.

53. A. Fröman and J.L. Kinsey Variational Treatment of Electronic and Mesonic Hydrogen Molecule Ions. November 1, 1960. (Published in Phys. Rev. 123, 2077, 1961).
54. A. Fröman Isotope Effects and Electronic Energy in Molecules. November 1, 1960. (Published in J. Chem. Phys. 36, 1490, 1962).
55. R. Pauncz, J. de Heer and P.O. Löwdin Studies on the Alternant Molecular Orbital Method. I. General Energy Expression for an Alternant System with Closed Shell Structure. November 1, 1960. (Published in J. Chem. Phys. 36, 2247, 1962).
56. R. Pauncz, J. de Heer and P.O. Löwdin ----- . II. Application to Cyclic Systems. November 1, 1960. (Published in J. Chem. Phys. 36, 2257, 1962).
57. Roy McWeeny Spin Polarization Effects in Paramagnetic Molecules. November 15, 1960.
58. Report from the International Summer Institute and Symposium in Quantum Chemistry held at Uppsala University, Uppsala, Sweden, July 17 - August 21, 1960.
59. Roy McWeeny On the Non-Orthogonality Problem for Interacting Electronic Systems. January 15, 1961.
60. Y. Öhrn and R. McWeeny Justification of the One-Body Model for an Electron Outside a "Core" With Applications to Lithium and Sodium. February 15, 1961.
61. Roy McWeeny Perturbation Theory for the Fock-Dirac Density Matrix. March 15, 1961. (Phys. Rev. 126, 1028, 1962).
62. Z.W. Ritter, R. Pauncz, and K. Appel Approximate Analytical Wave Functions for the $1s^2ns^2S_{1/2}$ States of Li and Li-Like Ions. April 15, 1961. (Published in J. Chem. Phys. 35, 571-575, 1961).
63. A. Fröman Comments on the Relativistic Corrections and the Electronic Correlation in the Li-Like Ions. June 1, 1961.
64. Per-Olov Löwdin Studies in Perturbation Theory. VI. Contraction of Secular Equations.
65. Per-Olov Löwdin ----- . VII. Localized Perturbation.
66. Klaus Appel Rational Approximation of Decay-Type Functions. October 1, 1961. (Published in Nordisk Tidskrift for Informationsbehandling, BIT, 2, 69, 1962).
67. Per-Olov Löwdin Band Theory, Valence Bond and Tight-Binding Calculations. October 15, 1961. (Published in J. Appl. Phys. 33, 251, 1962).

68. Per-Olov Löwdin The Normal Constants of Motion in Quantum Mechanics Treated by Projection Technique. November 15, 1961. (Revs. Modern Phys. 34, 520, 1962).
69. Jan Olof Nordling Successive Partitioning Technique for Solution of Secular Equations. December 1, 1961.
70. William H. Adams A Hartree-Fock Perturbation Method. December 1, 1961.
71. Jean-Louis Calais Permutation Symmetry of the Three-Electron Problem. December 1, 1961.
72. William H. Adams The Stability of Hartree-Fock States. December 15, 1961. (Phys. Rev. 127, 1650 (1962)).
73. Lajos B. Rédei Remarks on the Quantum Mechanical Interpretation of the Stark Effect in the Hydrogen Atom. December 15, 1961. (Physics Letters 1, 191, 1962).
74. Jan Linderberg Study of Atoms by Perturbation Theory. December 15, 1961. (J. Mol. Spectroscopy 9, 95-106, 1962).
75. Asgar Ali and Richard F. Wood Applications of localized perturbation technique. April 1, 1962.
76. William H. Adams Orbital theories of electronic structure. May 1, 1962.
77. Fukashi Sasaki Eigenvalues of Fermion Density Matrices. May 1, 1962
78. Janos Ladik and Klaus Appel The Energy Band Structure of Polynucleotides in the Hückel Approximation. May 15, 1962.
79. J. Ladik and K. Appel Investigation of the π Electron System of Uracil with Different Semiempirical Methods. June 1, 1962.
80. A.J. Coleman The Structure of Fermion Density Matrices. June 1, 1962.
81. Lajos B. Rédei Limits of error for the electronic density, spin density and atomic form factors in quantum mechanical calculations. July 15, 1962.
82. Ruben Pauncz Studies on the Alternant Molecular Orbital Method. IV. Generalization of the Method to States with Different Multiplicities. August 1, 1962.
83. P.O. Löwdin Some Recent Progress in the Quantum Theory of Many-Electron Systems. August 15, 1962.
84. Lars T. Hedin On the Theoretical Foundation of the One-Electron Approximation. September 1, 1962.

- T I G.G. Hall Permeation through a Spherical Shell.
September 20, 1958. (Published in J. Theoret.
Biol. 1, 18, 1961).
- T II L. Jansen Introduction to Statistical Mechanics.
February 20, 1959.
- T III L. Hedin and S.O. Lundqvist Introduction to the Field Theoretical Approach
to the Many-Electron Problem. November 15,
1960.
- T IV F. Berencz Electron Correlation in Calculations on H_2 .
(Lecture presented at the 3rd International
Summer Institute in Quantum Chemistry at
Uppsala, Sweden, 1960).
- J.I. Horváth New Aspects of Quantum Mechanical Theory of
the Many-Body Problem. (Lecture presented
at the 3rd International Summer Institute in
Quantum Chemistry at Uppsala, Sweden, 1960).
- T V A.J. Coleman A note on nilpotent operators, Jordan canonical
form, Segré characteristics and minimal
polynomials. (Note prepared for the 4th International
Summer Institute in Quantum Chemistry at Uppsala,
Sweden 1962.)

<p>Uppsala University, Sweden Quantum Chemistry Dept Rep. No. AD</p> <p>Monitoring Agency: USAF, EOOAR</p> <p>Field: Physics</p> <p>APPLICATIONS OF LOCALIZED PERTURBATION TECHNIQUE.</p> <p>M. Asgar Ali and Richard F. Wood April 1, 1962</p> <p>ABSTRACT: Applications have been made of the localized perturbation technique for conjugated systems within Hückel theory by using the inverse of cyclic matrices in terms of Chebyshev polynomials.</p>	<p>Contract: AF 61 (052)-351 TN 75</p> <p>Uppsala University, Sweden Quantum Chemistry Dept Rep. No. AD</p> <p>Monitoring Agency: USAF, EOOAR</p> <p>Field: Physics</p> <p>APPLICATIONS OF LOCALIZED PERTURBATION TECHNIQUE.</p> <p>M. Asgar Ali and Richard F. Wood April 1, 1962</p> <p>ABSTRACT: Applications have been made of the localized perturbation technique for conjugated systems within Hückel theory by using the inverse of cyclic matrices in terms of Chebyshev polynomials.</p>
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